A DYNAMIC MECHANICAL CHARACTERIZATION

OF POLYCARBONATE

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A DYNAMIC MECHANICAL CHARACTERIZATION OF POLYCARBONATE

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NOMENCLATURE

Latin Letters

Symbol	Definition	Units
a	Axial displacement in Visco-Elastic Tester	in.
a_T	Ratio of relaxation times at two different temperatures	--
a_M	Ratio of relaxation times at two different molecular weights	--
C_1^g, C_2^g	Coefficients in WLF equation referred to T_g as reference	deg.
C_1^o, C_2^o	Coefficients in WLF equation referred to T_o as reference	deg.
F_x	Force measurement in X direction	dyne
F_y	Force measurement in Y direction	dyne
f_o/B	Fractional free volume at reference temperature, T_o	--
$G(t)$	Shear relaxation modulus	dynes/cm^2
G^*	Complex dynamic shear modulus	dynes/cm^2
G'	Shear storage modulus	dynes/cm^2
G''	Shear loss modulus	dynes/cm^2
G_e	Shear equilibrium modulus	dynes/cm^2
G_i	Modulus contribution of model element	dynes/cm^2
h	Sample thickness	in.
J	Creep compliance	cm^2/dyne
J_i	Compliance contribution of model element	cm^2/dyne
M	Molecular weight	g/mole
$\overline{M}_w$	Weight average molecular weight	g/mole
$\overline{M}_n$	Number average molecular weight	g/mole

NOMENCLATURE (continued)

Symbol	Definition	Units
M_R	Reference molecular weight	g/mole
R	Universal gas constant	$ergK^{-1}mol^{-1}$
r	Radius of eccentric disc	in.
t	Time	sec.
	Greek Letters	
$\alpha_{f/B}$	Thermal expansion of free volume relative to total volume	$deg.^{-1}$
γ_o	Shear strain amplitude	--
$\dot{\gamma}$	Rate of shear strain	$sec.^{-1}$
η_a	Apparent shear viscosity	poise
η^*	Complex, dynamic shear viscosity	poise
η'	Real part of complex viscosity	poise
η_o	Zero shear viscosity	poise
λ_1	Terminal relaxation time	sec.
μ	Relaxation time	sec.
ρ	Density	g/cm^3
τ	Shear stress	$dyne/cm^2$
χ_M	Shift factor introduced by Mendelson based on terminal relaxation time	--
ω	Frequency	radians/sec.

CHAPTER I

INTRODUCTION

Plastic connecting devices are integral parts of communications systems networks. Metal connectors which serve as terminating and connecting devices for telephone cables and associated communications equipment are protected with plastic modules. Assuring the integrity of the plastic component decreases maintenance costs and increases customer satisfaction. Proper functioning of the total communications network depends on many factors, one of which is the ability of the plastic module to insulate metal connectors from ground, thus maintaining electrical continuity. Should the plastic module fail, the electrical continuity could be lost resulting in diminished quality of the total system.

Since all polymers exhibit viscoelastic behavior, valuable information can be obtained through an investigation of the polymers' viscoelastic properties. Viscoelastic behavior means that a material exhibits liquid-like and solid-like characteristics. Hooke's law deals with the mechanical properties of elastic solids, for which the stress is directly proportional to the strain in small deformations, but independent of the strain rate. The liquid-like viscous characteristics may be described from classical hydrodynamics in accordance with Newton's law which states that the stress is directly proportional to the strain rate but independent of the strain itself. Deviation from ideal behavior occurs when (1) finite strains are imposed on a solid and the stress-strain relations become non-Hookean, or similarly in steady flow under finite strain rates many fluids exhibit non-Newtonian flow, or (2) even if strain or strain rates are infinitesimal a system may exhibit solid-like and liquid-like behavior simultaneously.

This solid and liquid-like behavior can be treated using models combining Newton's and Hooke's laws. A Maxwell element which combines a spring (Hookean) and dashpot (Newtonian) in series may be used as the basis for a model; a Voigt element which employs a spring and dashpot in parallel may also be used. Each element has associated with it a discrete relaxation (or retardation for Voigt element) time, μ, associated with the shear modulus G. The relaxation or retardation time μ is defined as the viscosity (from the dashpot) divided by the shear modulus of the spring. A single element alone (whether Maxwell or Voigt) does not approach the behavior of a real system. It is necessary, therefore, to combine several elements in parallel from which one obtains a distribution of relaxation (Maxwell elements in parallel) or retardation times (Voigt elements in series). A group of Maxwell elements in parallel is representative of a discrete spectrum of relaxation times where each relaxation time, μ_i, is associated with the spectral strength or modulus of each element, G_i. Likewise, for a model of Voigt elements in series, a distribution of retardation times is obtained for which μ_i is associated with spectral compliance, J_i. The viscoelastic functions of modulus compliance and viscosity (for a model composed of a number of elements, whether in series or parallel) are obtained by summation of the functions over all elements. Boltzmann's[1] superposition principle states that the effects of mechanical history are linearly additive when stress is described as a function of history of strain or strain rates, or conversely when the strain is expressed as a function of the historical rate of change of stress. The mechanical history is only additive given that the material is linerarly viscoelastic.This may be manifested in an experiment where the ratio of stress to strain is a function of time alone, and not of the stress magnitude.

The relationships for interconversion of the viscoelastic function are based upon Boltzmann's superposition principle which is valid if the system exhibits linear viscoelastic behavior.[2] For example, in transient measurements the creep compliance and relaxation modulus are related as follows for a linear system:

$$\int_0^t G(\mu)J(t-\mu)d\mu=t \qquad (1)$$

$$\int_0^t J(\mu)G(t-\mu)d\mu=t \qquad (2)$$

Given the above relationships and having one function given analytically the other function can be calculated by numerical evaluation of the above convolution integrals. Alternatively, the Laplace transform of the G(t) and J(t) are related reciprocally and may be calculated as follows:

$$pL\left[J(t)\right]=\frac{1}{p}\left[LG(t)\right] \qquad (3)$$

The Boltzmann principle of superposition may be applied to any of the viscoelastic functions provided linear behavior is exhibited. Given that viscoelastic functions are interrelated (in linear viscoelastic systems) time-temperature superposition as it applies to one viscoelastic function is applicable to other viscoelastic functions. This may be shown by a close examination of Boltzmann's superposition principle. Expressed in terms of simple shear, if a stress, τ, is applied at time, t=0, the strain function at time t is given by:

$$\gamma(t)=\tau_o J(t) \qquad (4)$$

If a larger stress is applied the effects are additive:

$$\gamma(t)=(\tau_0+\tau_1)J(t) \tag{5}$$

If τ_0 is applied at t=0 and additional stress τ_1 is applied at time, t_1, the strain function will be:

$$\gamma(t)=\tau_0 J(t)+\tau_1 J(t-t_1) \tag{6}$$

which is merely the linear superposition of two strains at their respective elapsed times. The many possible variations of loading history may be generalized as follows:

$$\gamma(t)=\Sigma\tau_i J(t-t_i) \tag{7}$$

This example of superposition was shown for compliance but might just have easily been applied to stress relaxation modulus or dynamic modulus.

Dynamic mechanical properties were chosen for this investigation as the viscoelastic functions to describe the mechanical properties of the polycarbonate plastic materials used in connector modules. The polycarbonate system was found to be linear up to strains of 20%. This linearity was established as discussed in Chapter III.[8] Master curves were established over which loss moduli, storage moduli and dynamic viscosity can be examined over a broad frequency range. These curves may be used as criteria for comparing various lots of polycarbonate for uniformity of properties, for establishing if processing of the polycarbonate into components has altered the molecular weight or determining if subsequent field exposure or aging has altered the mechanical properties of polycarbonate.

Some information on the dynamic mechanical properties of polycarbonate has been published, thus, this investigation will add to that body of knowledge and will increase our understanding of the properties of this important engineering plastic.

Four molecular weight samples of polycarbonate were characterized using a Visco-Elastic Tester (marketed by Rheometrics, Inc.) to determine shear components of storage and loss moduli as a function of rotational frequency over a temperature range approaching processing conditions (458-533^{o}K). Complex dynamic viscosity was calculated from loss and storage moduli data.

Master curves were constructed from the moduli data to reference temperature and reference molecular weight by graphically shifting the curves horizontally (i.e., logarithmically with respect to the frequency abscissa). That the moduli curves should shift horizontally is a well known fact in the literature.[18] The method by which dynamic viscosity shifts has not been recognized quite as clearly. Formulae[4] are derived in this investigation for shifting dynamic viscosity from a knowledge of moduli shifting. These shift formulae require that logarithmic shifts be made with respect to the frequency abscissa and the viscosity ordinate. The shifts are equal to each other and are also equal to the graphical shifts made in shifting moduli data. All shifting depends upon polycarbonate following a linear viscoelastic constraint.

J. D. Ferry[1] shows basic shapes over broad frequency ranges for master curves of loss and storage moduli and dynamic viscosity for a high molecular weight amorphous polymer (poly-n-octyl methacrylate). These curves are shown in Figures 1-3. The portion of the curves over which the data from this investigation were taken is shown as the dashed part of the curves.

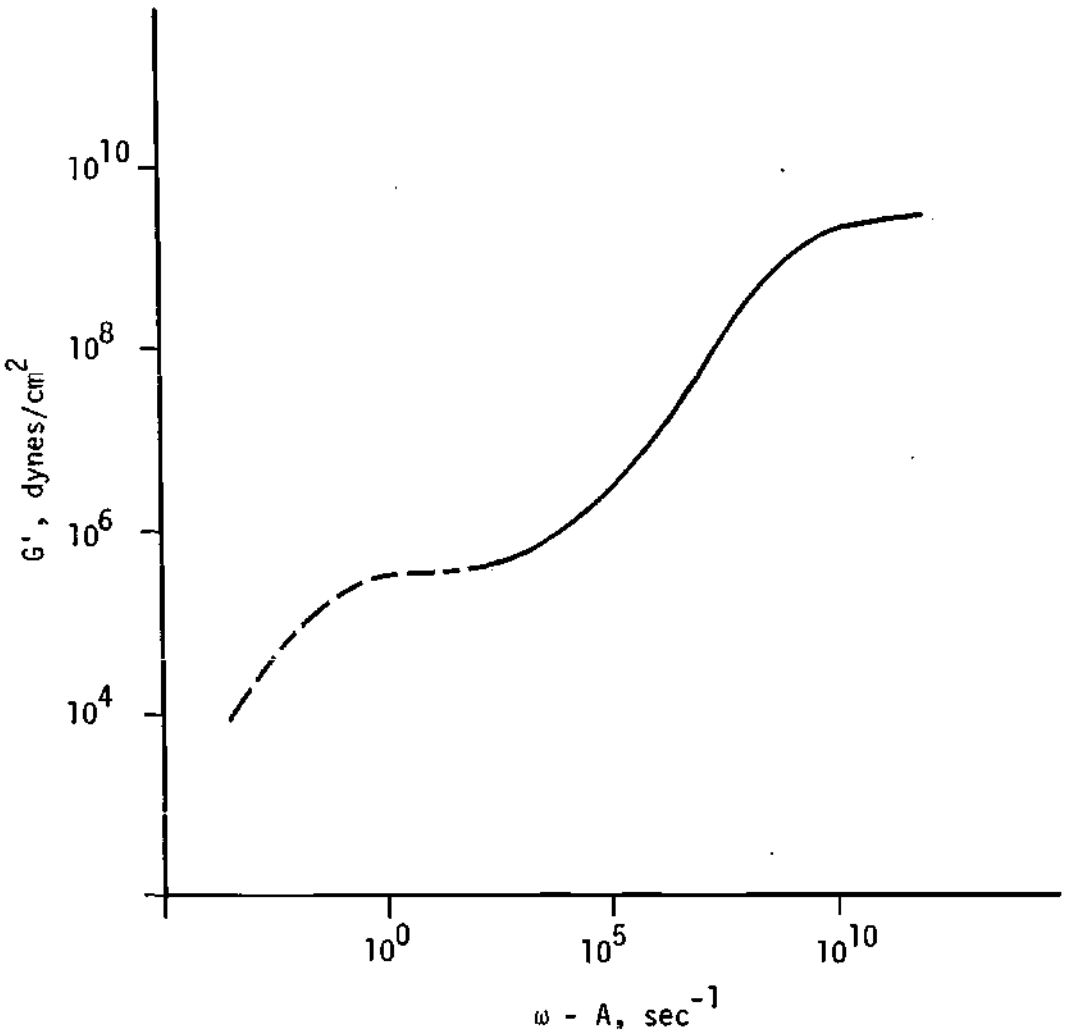


Figure 1. Storage Modulus vs. Reduced Frequency for a High Molecular Weight Amorphous Polymer (fractionated poly-n-octyl methacrylate)[2]

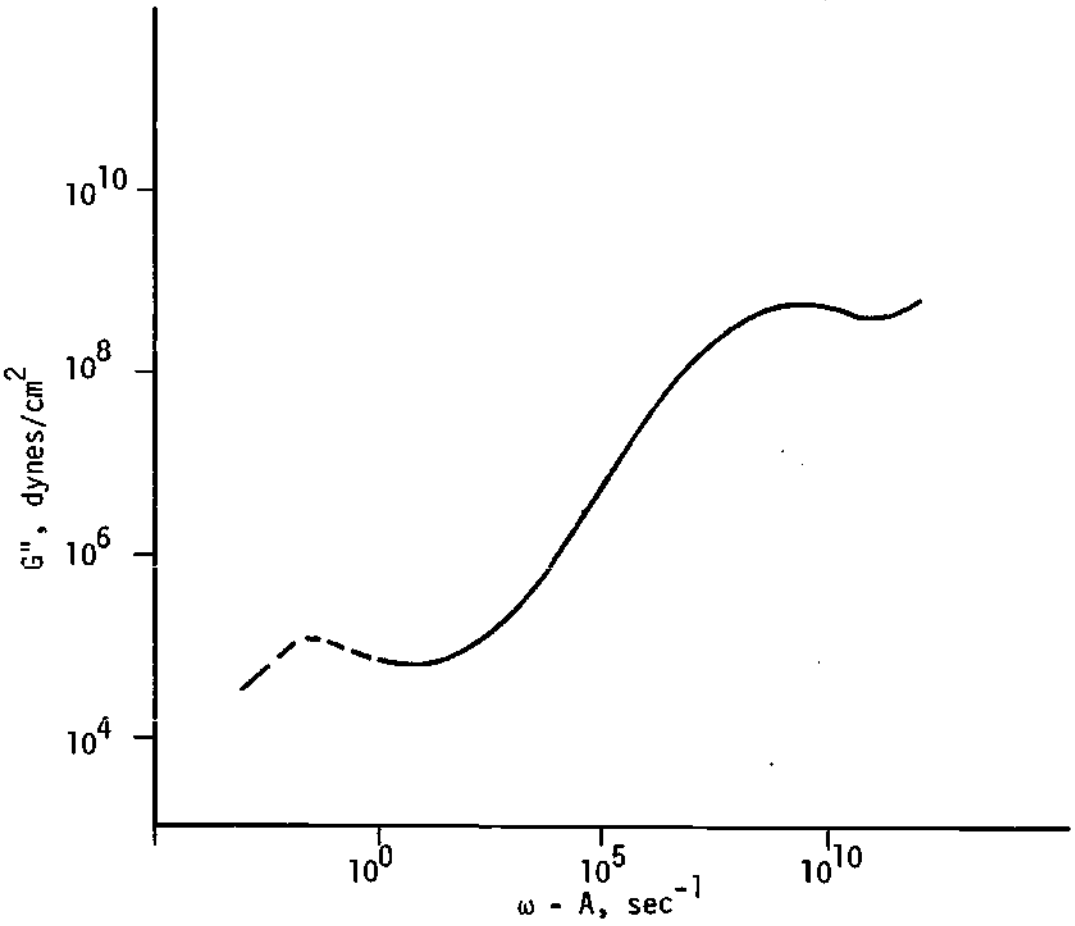


Figure 2. Loss Modulus vs. Reduced Frequency for a High Molecular Weight Amorphous Polymer (fractionated poly-n-octyl methacrylate)[2]

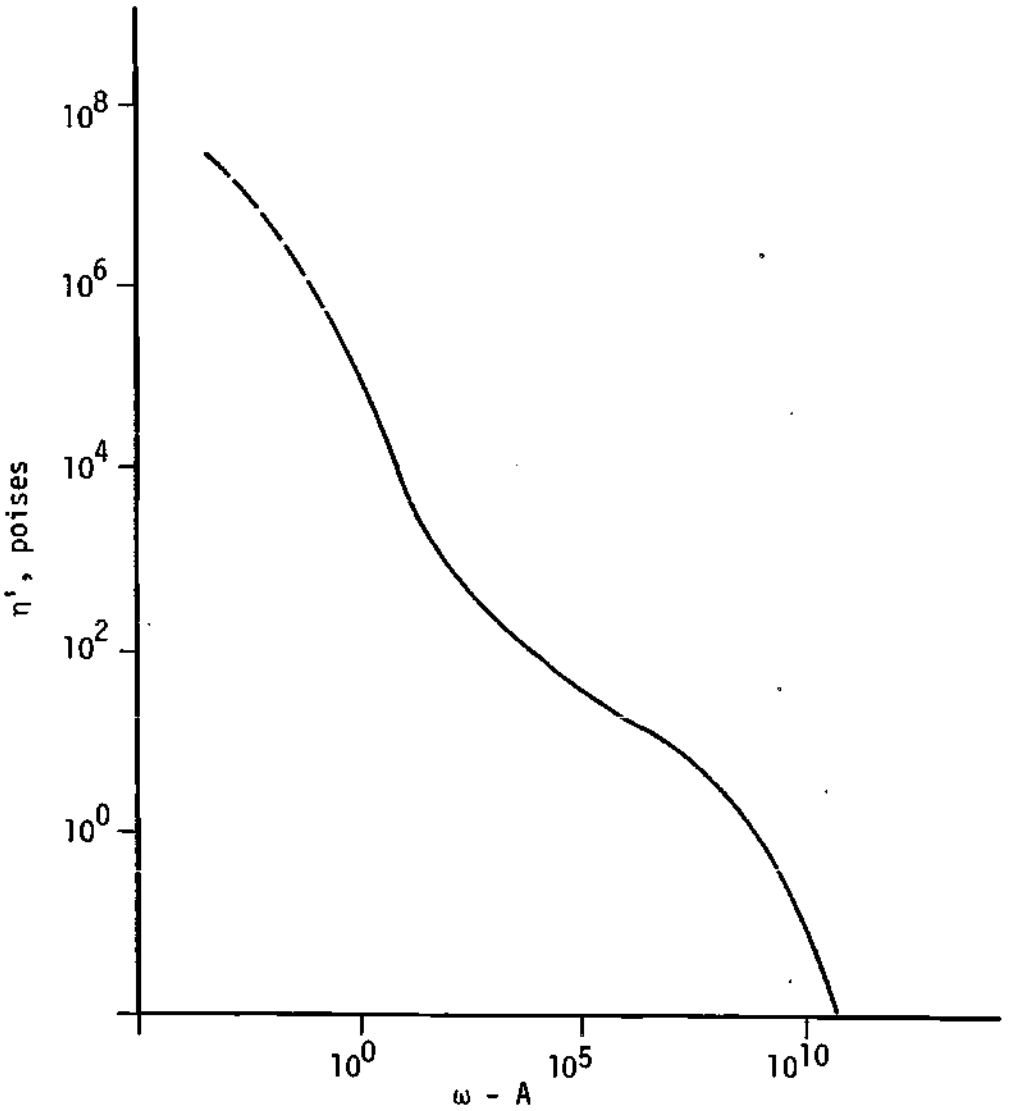


Figure 3. Dynamic Viscosity vs. Reduced Frequency for a High Molecular Weight Amorphous Polymer (fractionated poly-n-octyl methacrylate)[2]

CHAPTER II

THEORY

In order to begin to understand the functions of the dynamic shear modulus and dynamic viscosity and their relationships to the materials properties it is necessary to understand the mathematical origin and interrelationship between these and other viscoelastic functions. Thus, this chapter attempts (1) to define the dynamic shear modulus in terms of shear stress and shear strain and also in terms of the shear relaxation modulus, (2) to develop time, temperature and molecular weight shifting of dynamic moduli, (3) to define the complex dynamic viscosity in terms of the dynamic modulus and frequency, and (4) to develop time, temperature and molecular weight shifting of dynamic viscosity from a knowledge of moduli shifting. In order to develop these goals most logically the chapter was divided into sections for the dynamic shear modulus and complex dynamic viscosity.

A. Dynamic Shear Modulus

The response of polymeric materials to a shear deformation may be determined as follows:[2]

$$\tau(t)=\int_0^t G(t-t')\,\frac{d\gamma}{dt'}\,dt' \qquad (8)$$

Where τ is the shear stress, t is time, G is the shear relaxation modulus and γ is the shear strain. Equation (8) is valid within the linear viscoelastic range of strains, i.e., strains for which G is a function of time only, not stress or strain. Subjecting the system to an oscillatory shear strain of the form:

$$\gamma(t)=\gamma_0 e^{i\omega t} \qquad (9)$$

where γ_o is the shear strain amplitude and ω is the frequency in radians per second, results in the following equation:

$$\tau(t)=\left[i\omega\int_0^\infty G(t)\, e^{-i\omega t}\, dt\right]\gamma(t) \qquad (10)$$

For the purposes of this investigation shear strain was introduced using eccentric rotating disc geometry.

The bracketed term in equation (10) is defined as the complex dynamic shear modulus, G*, and may be written into equation (10) as follows:

$$\tau(t)=G^*(\omega)\gamma(t) \qquad (11)$$

The complex dynamic shear modulus is a measure of a plastic materials' response to a unit of oscillatory shear strain, and may be represented analytically as follows:

$$G^*=G'+iG'' \qquad (12)$$

Where G' is the storage modulus, G" is the loss modulus and $i=\sqrt{-1}$. The loss and storage moduli may be substituted into equation (11) as follows:

$$\tau(t)=G'\gamma(t)+iG''\gamma(t) \qquad (13)$$

Taking the first derivative of $\gamma(t)$ results in the following equation:

$$\dot{\gamma}(t)=\gamma_o i\omega e^{i\omega t} \qquad (14)$$

Which, by substituting in equation (9), results in the following:

$$\dot{\gamma}(t)=i\omega\gamma(t) \qquad (15)$$

Which may be substituted into equation (13) to obtain this analytical expression describing the relationship between loss and storage moduli and shear stress:

$$\tau(t)=G'\gamma(t)+G''\dot{\gamma}(t)/\omega \qquad (16)$$

Equations (12)-(16) are commonly used in discussing viscous and elastic contributions separately. It is important to realize that equations (12), (13) and (16) are merely convenient representations, and independent treatment of the materials' response components (i.e., G', G") results in an incomplete characterization of the materials properties.

In order to obtain G* over a wider than experimentally accessible frequency range, principles of superposition may be applied. The simple frequency-temperature superposition used here is only applicable within the linear viscoelastic range of behavior. Application of such techniques were used here to extend a three decade experimental range to five decades.

The effect of raising the temperature is to accelerate molecular, segmental motion responsible for viscoelastic processes. The effect of temperature may be expressed in terms of a ratio, a_T, of the time constant or relaxation time, μ, at temperature, T, to its value μ_o at a reference temperature T_o. This may be illustrated for the simple case of a Maxwell model in a stress relaxation experiment. The force on each element relaxes exponentially and may be expressed as:

$$\sigma=\sigma_o e^{-t/\mu} \tag{17}$$

in which the relaxation time μ is defined as:

$$\mu=\eta/G \tag{18}$$

where η is the viscosity and G the modulus.

The function, a_T, is defined as follows:

$$\mu=a_T\mu_o \tag{19}$$

and may be substituted into equation (17) to give:

$$\sigma=\sigma_o e^{-t/a_T\mu_o} \tag{20}$$

a_T is a temperature dependent viscosity function which contains all the information for relaxation time changes resulting from temperature variations.

It is common practice to define t/a_T as the reduced time. In many cases frequency and temperature affect viscoelasticity only through a_T (known as a shift factor) resulting in a logarithmic shift of moduli, for example, with respect to frequency. In an analogous manner isotherms of loss and storage moduli as a function of frequency may be shifted graphically with respect to frequency to a reference temperature, T_o as follows:

$$G'(\omega,T)=G'(\omega a_T,T_o) \tag{21}$$

$$G''(\omega,T)=G''(\omega a_T,T_o) \tag{22}$$

Often a vertical shift is applied that accounts for stiffening due to rubber elasticity. It is proportional to the logarithm of the ratio of the temperatures in the range of interest. The largest vertical shift which could be expected over the temperature range of this investigation was calculated using the highest and lowest temperatures over which testing was done. This vertical shift was found to amount to 0.08 decade, sufficiently small to be considered negligible.

In a manner similar to the development of the shift factor, a_T, a shift factor a_M can be developed for shifting to a reference molecular weight. Since increasing the molecular weight increases relaxation times in the plateau and flow regions, an analytical expression can be written in terms of a ratio of relaxation times at any given molecular weight and reference molecular weight as follows:[2]

$$\mu=a_M\mu_o \tag{23}$$

Molecular weight is considered to affect viscoelasticity through the function

a_M resulting in a logarithmic shift, with respect to frequency, to a reference molecular weight as follows:

$$G'(\omega,T,M)=G'(\omega a_T a_M,T_o,M_o) \tag{24}$$

$$G''(\omega,T,M)=G''(\omega a_T a_M,T_o M_o) \tag{25}$$

B. Complex Dynamic Viscosity

The complex dynamic viscosity is a property derivable from the complex shear modulus and is an oscillatory response analog to steady flow viscosity.

In a manner analogous to viscosity in the steady flow case, the complex dynamic viscosity is defined as:

$$\tau=\dot{\gamma}\eta^* \tag{26}$$

Equating equation (26) and equation (11) and using equation (15) one obtains:

$$\dot{\gamma}\eta^*=\gamma G^* \tag{27}$$

$$i\omega\gamma\eta^*=\gamma G^* \tag{28}$$

$$\eta^*=G^*/i\omega \tag{29}$$

Substituting the definition of G* in terms of storage and loss moduli from equation (12) gives:

$$\eta^*=\frac{G'+iG''}{i\omega} \tag{30}$$

Since $1/i=-i$, then equation (30) becomes:

$$\eta^*=\frac{G''-iG'}{\omega} \tag{31}$$

By definition:

$$\eta'=G''/\omega \tag{32}$$

and

$$\eta''=G'/\omega \tag{33}$$

so that

$$\eta^* = \eta' - i\eta'' \tag{34}$$

and

$$|\eta^*| = \frac{\sqrt{(G')^2 + (G'')^2}}{\omega} \tag{35}$$

In the literature η' is commonly referred to as the dynamic viscosity. Independent treatment of components of complex quantities is invalid since it omits a portion of the materials properties. Complex dynamic viscosity may be calculated from loss and storage moduli at a given frequency using equation (35).

Isotherms of the complex dynamic viscosity as a function of frequency may be shifted into master curves for each molecular weight at a reference temperature T_o by the shift formulae developed below:[4]

By definition:

$$|\eta^*(\omega,T)| = \frac{|G^*(\omega,T)|}{\omega} \tag{36}$$

Knowing that the complex modulus shifts as follows:

$$G^*(\omega,T) = G^*(\omega a_T, T_o) \tag{37}$$

and substituting equation (37) into equation (36) one obtains:

$$|\eta^*(\omega,T)| = \frac{|G^*(\omega a_T, T_o)|}{\omega} \tag{38}$$

Applying a horizontal shift, a_T, with respect to frequency in equation (36) results in:

$$|\eta^*(\omega a_T, T_o)| = \frac{|G^*(\omega a_T, T_o)|}{\omega a_T} \tag{39}$$

By substituting equation (38) into equation (39) one obtains:

$$|\eta^*(\omega a_T, T_o)| = \frac{|\eta^*(\omega,T)|}{a_T} \tag{40}$$

which upon rearrangement gives:

$$\eta^*(\omega,T)=a_T\eta^*(\omega a_T,T_o) \qquad (41)$$

Given the above shift formulae, the viscosity versus frequency isotherms may be shifted analytically along the frequency abscissa and viscosity ordinate by the same log a_T magnitude obtained in the graphical shifting of loss and storage moduli data.

By the same principles used to develop shift formulae for shifting complex dynamic viscosity to a reference temperature, it is possible to generate shift formulae for shifting the reduced viscosity versus reduced frequency curves to a reference molecular weight as follows:[4]

$$\eta^*(\omega,T,M)=a_T a_M \eta^*(\omega a_T a_M,T_o,M_o) \qquad (42)$$

In a manner comparable to the time-temperature shifting, the molecular weight shifting (as prescribed in equation 42) is accomplished by analytical shifts along the log frequency abscissa and log viscosity ordinate by the same log a_M determined in the graphical shifting of loss and storage moduli data.

The usefulness of such master curves for characterization of polycarbonate and comparison to other polycarbonates will be discussed in a subsequent chapter.

In summary, definitions have been developed which describe dynamic shear moduli and dynamic viscosity. It was shown how the dynamic shear modulus is related to the shear relaxation modulus, G(t), and how the dynamic viscosity may be calculated from the dynamic shear modulus. Shifting was described for the purpose of expanding the frequency range of the dynamic modulus or dynamic viscosity at any given temperature. Shift formulae were developed for shifting dynamic moduli isotherms into master curves at a

reference temperature and reference molecular weight. Also shift formulae were developed for shifting dynamic viscosity and it was shown mathematically that analytical shifts of equal magnitude were necessary along the frequency abscissa and the viscosity ordinate and that the shift magnitudes must equal the logarithmic horizontal shift for reduction of dynamic moduli isotherms.

CHAPTER III

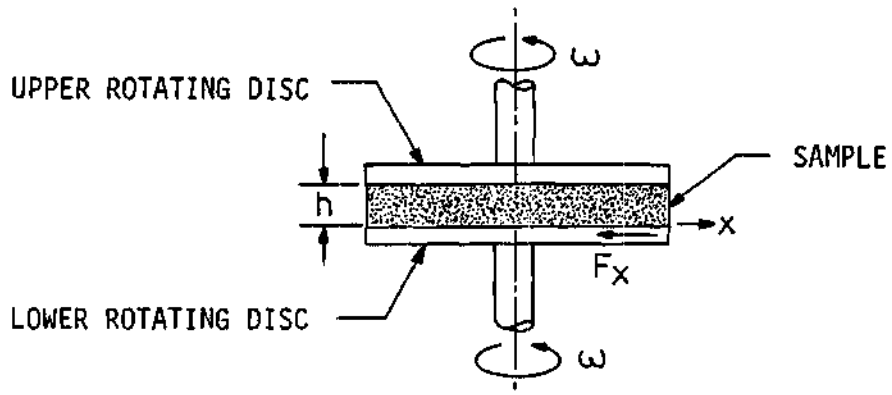
EXPERIMENTAL

The purpose of this chapter is to describe in detail the theory and operation of the test apparatus used in this investigation and the preparation of the various molecular weight samples for testing.

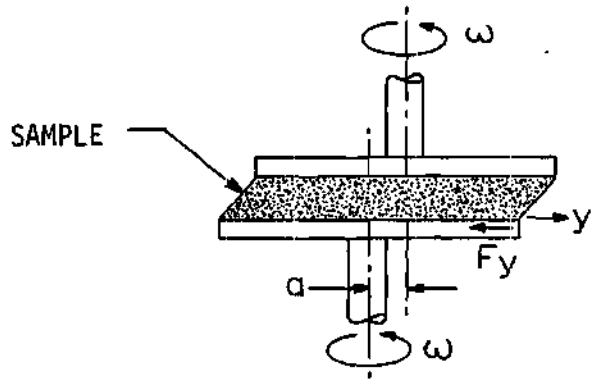
A. Test Apparatus - Theory and Operation

The Visco-Elastic Tester, marketed by Rheometrics, Inc., was chosen for this investigation for a multiplicity of reasons. Simplicity of operation, versatility and precision make it a valuable and exceptional tool for rotational rheometry. A microcomputer built into the instrument averages viscous and elastic force components independently over each cycle and reads out directly in loss and storage modulus at a given frequency. It is quite versatile in that it covers a fairly broad frequency range, 0.1-100 $sec.^{-1}$ and a substantial temperature range, 175-600K. Both frequency and temperature ranges are broader in the Visco-Elastic Tester than with the Weissenberg Rheogoniometer or the Rheovibron. In addition, the Visco-Elastic Tester is far simpler to operate than either of the aforementioned instruments. Rapid equilibrium upon changing temperatures is another asset of the Visco-Elastic Tester.

The apparatus shown schematically in Figure 4 was used to determine shear moduli components G' and G" as functions of rotational frequency, ω, and temperature, through a knowledge of eccentric rotating disc geometry. In this test, two circular discs of radii r rotate about parallel axes which have been displaced by an amount designated as "a", shown in the schematic diagram (Figure 4). A sample of thickness "h" is confined between the discs and is forced through a shear deformation cycle with each revolution, as a result of the eccentricity.[5]



FRONT VIEW



SIDE VIEW

Figure 4. Schematic of Test Apparatus Illustrating the Forcing of the Sample Through a Shear Cycle with each Revolution.

Referring to Figure 4, as the discs rotate 90^0, elements of the sample undergo a shear deformation which is illustrated in the side view. This shear strain results in a shear force on the surface of each disc. The elastic component in phase with that force, F_y, tends to restore the sample to its undeformed state. It is a measure of the energy stored and may be used to calculate the elastic or storage modulus G' as simply the stress $F_y/\pi r^2$, divided by the strain, a/h,

$$G' = \frac{F_y/\pi r^2}{a/h} \tag{43}$$

Since polymeric materials also dissipate energy, there is a viscous component of the shear force, F_x, which is a measure of the energy loss. The loss or viscous modulus is the stress, $F_x/\pi r^2$, 90^0 out of phase with the applied shear strain divided by the strain and is calculated as:

$$G'' = \frac{F_x/\pi r^2}{a/h} \tag{44}$$

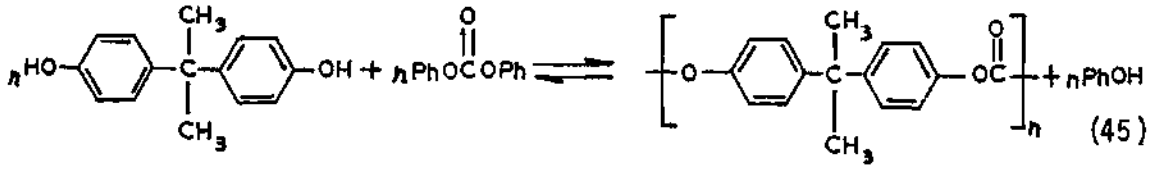
A biaxial force, strain gage transducer[5] in the apparatus measures F_x and F_y. This is done four times in one cycle with the displacement "a" in the positive y direction and again four times with "a" in the negative direction. A microcomputer, which is dedicated to the apparatus, averages the eight readings, performs the calculations as indicated above and displays G' and G". The device automatically scans frequency sequentially at a set temperature.

B. Sample Preparation and Identification

Four molecular weight distributions of bisphenol A polycarbonate were investigated. The weight average ($\bar{M}_w$) and number average ($\bar{M}_n$) molecular weights and polydispersities ($\bar{M}_w/M_n$) were determined using a Waters gel

permeation chromatograph.[6] These values are given in Table 1. Samples were identified as A, B, C and D and are commercially available bisphenol A polycarbonates currently in use in the communications field in connector modules.

Polycarbonate is produced commercially by an ester interchange reaction carried out in the melt between 4, 4-isopropylidene diphenol (bisphenol A) and diphenyl carbonate as follows:



Pellets from each of the four molecular weight distributions were dried in an oven at 125 C for 12 hours to remove most labile moisture present. Drying is necessary since polycarbonate is a hygroscopic material which undergoes hydrolytic degradation in the presence of water at elevated temperatures.[7]

After drying, each sample was compression molded into plaques at 300°C in a brass mold to a thickness of 0.100 inch. Circular samples, one inch in diameter, were pressed from plaques to give specimens of proper dimensions for testing on the Visco-Elastic Tester. Immediately prior to testing, the circular samples were dried at 125 C for 12 hours to remove labile moisture absorbed between molding and testing.

A disc of each sample was placed between the circular rotating discs of the apparatus and pressed to a fixed thickness. Serrated discs were used to assure optimum mating between the discs and the surface of the sample.

Table 1. Molecular Weight Data for Samples A, B, C and D

Molecular Weight Sample	Number Average Molecular Weight $\bar{M}_n$	Weight Average Molecular Weight $\bar{M}_w$	Polydispersity $\bar{M}_w/\bar{M}_n$ D
A	11,700	26,900	2.30
B	13,000	32,400	2.50
C	14,100	36,300	2.58
D	16,700	40,400	2.42

The instrument was programmed to scan frequency at the lowest possible test temperature above the glass transition temperature of the material while remaining within the mechanical limitations of the instrument. The upper range of the Visco-Elastic Tester is approximately 10^6 dynes/cm^2, and it operates over a frequency range of 0.1-100 sec^{-1}. Viscous and elastic shear components G" and G' were determined as functions of rotational frequency, ω, over a temperature range of approximately 170-260^{o}C for each molecular weight sample. D. L. Reinhard reports that magnitudes of G' and G" for bisphenol A polycarbonate were invariant up to shear strain levels of 20%[8]. Therefore, in this particular study using 5% shear strain amplitude, the shear properties may be considered linearly viscoelastic.

CHAPTER IV

RESULTS AND DISCUSSION

This chapter covers shifting of dynamic moduli and dynamic viscosity versus frequency isotherms into master curves at a reference temperature and molecular weight according to the mathematical relationships developed in the theory section. Constants are calculated to allow shifting to other temperatures and for comparison with universal constants and the data of other investigators. Additionally, comparisons are made between data reduction procedures described here and those used by other investigators.

The purpose of shifting dynamic moduli and dynamic viscosity data to a reference temperature and reference molecular weight is to examine the data over a broader frequency range than is normally available from isothermal data. It is simple and fast to shift the master durves to other reference temperatures where moduli and viscosity data may be examined. All shifting is based upon polycarbonate being linearly viscoelastic.

A. Time - Temperature Superposition

1. Dynamic Shear Modulus

A family of curves was generated for each of the four molecular weight distributions, at temperatures between 170-260^{o}C, by plotting storage and loss moduli as a function of frequency, ω. These curves are shown for molecular weight distributions A, B, C and D as Figures A-1-A-4 for storage modulus isotherms and B-1-B-4 for loss modulus isotherms in Appendices A and B. The data were shifted graphically, horizontally, that is, with respect to the time abscissa, into master curves at T_o=200^{o}C using the relationships developed in equations (21) and (22):

$$G'(\omega,T)=G'(\omega a_T,T_o) \tag{21}$$

$$G''(\omega,T)=G''(\omega a_T,T_o) \tag{22}$$

The master curves for each molecular weight are shown in Figures 5 and 6. Shifting all data horizontally by a shift factor a_T resulted in good master curves with little scatter of data. The maximum vertical shift which could be expected was calculated from expected rubber elasticity and found to amount to only 8/100 of a decade shift for the temperature range over which the data were obtained; this was considered to be sufficiently small to be neglected. A plot of the shift factors, a_T, resulting from experimentally shifting loss and storage moduli data into master curves T-200°C is shown in Figure 7.

Shifting the data into master curves allows inspection and comparison of each material's dynamic mechanical behavior over a broad frequency range for a particular reference temperature. Loss and storage moduli shifted identically for any given molecular weight into master curves.

Shift factors from G' and G" for all molecular weights were fitted to a linear transform of a least squares hyperbolic plot of the form:

$$\log a_T = \frac{(T-T_o)}{A+B(T-T_o)} \tag{46}$$

This resulted in a single expression which when compared to the WLF equation the coefficients C_1^o and C_2^o may be calculated as follows:

$$\log a_T = \frac{T-T_o}{-\frac{C_2^o}{C_1^o} - \frac{1}{C_1^o}(T-T_o)} \tag{47}$$

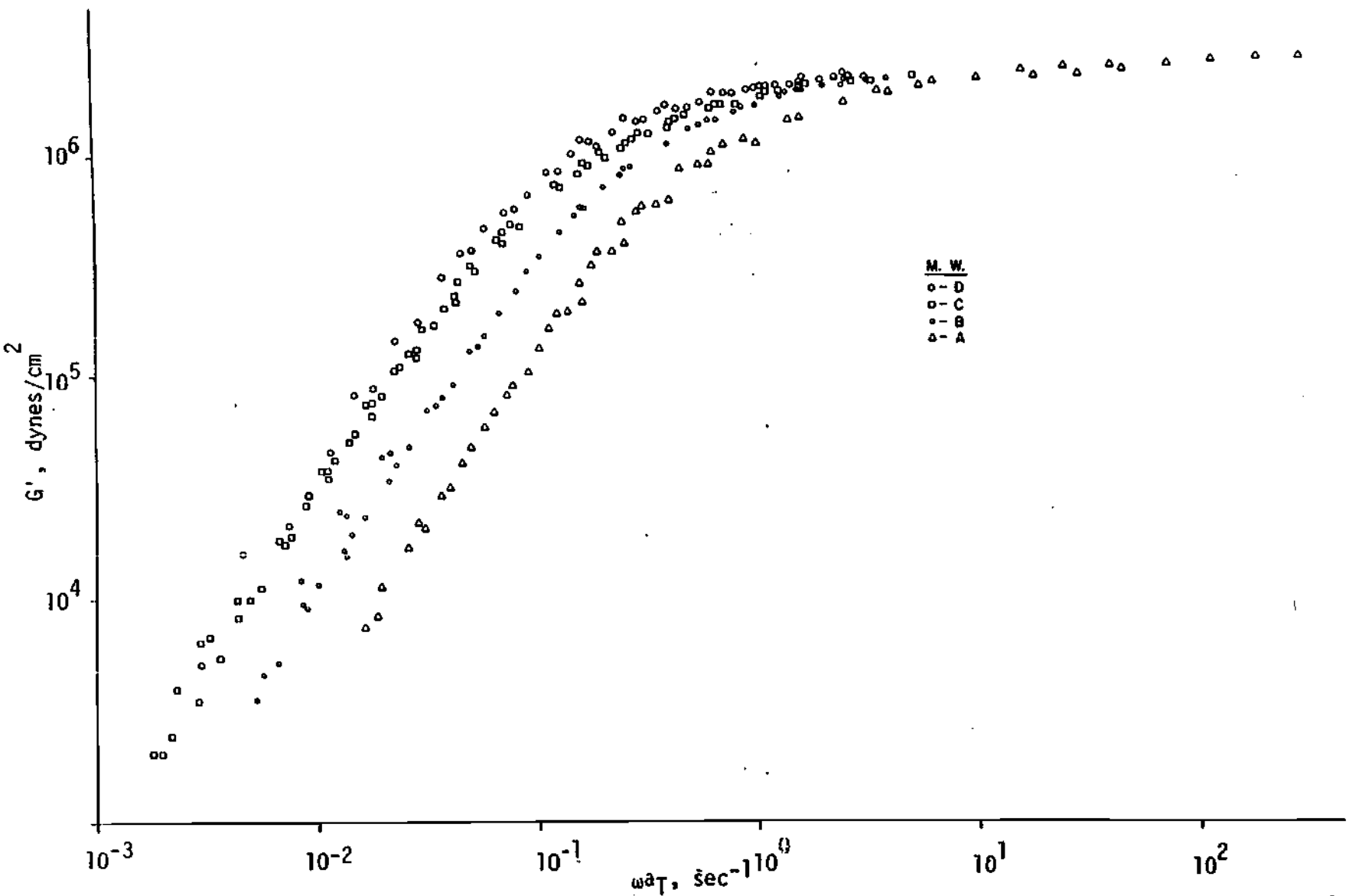


Figure 5. Storage Modulus Master Curves vs. Reduced Frequency at Reference Temperature, T_o = 473^{o}K

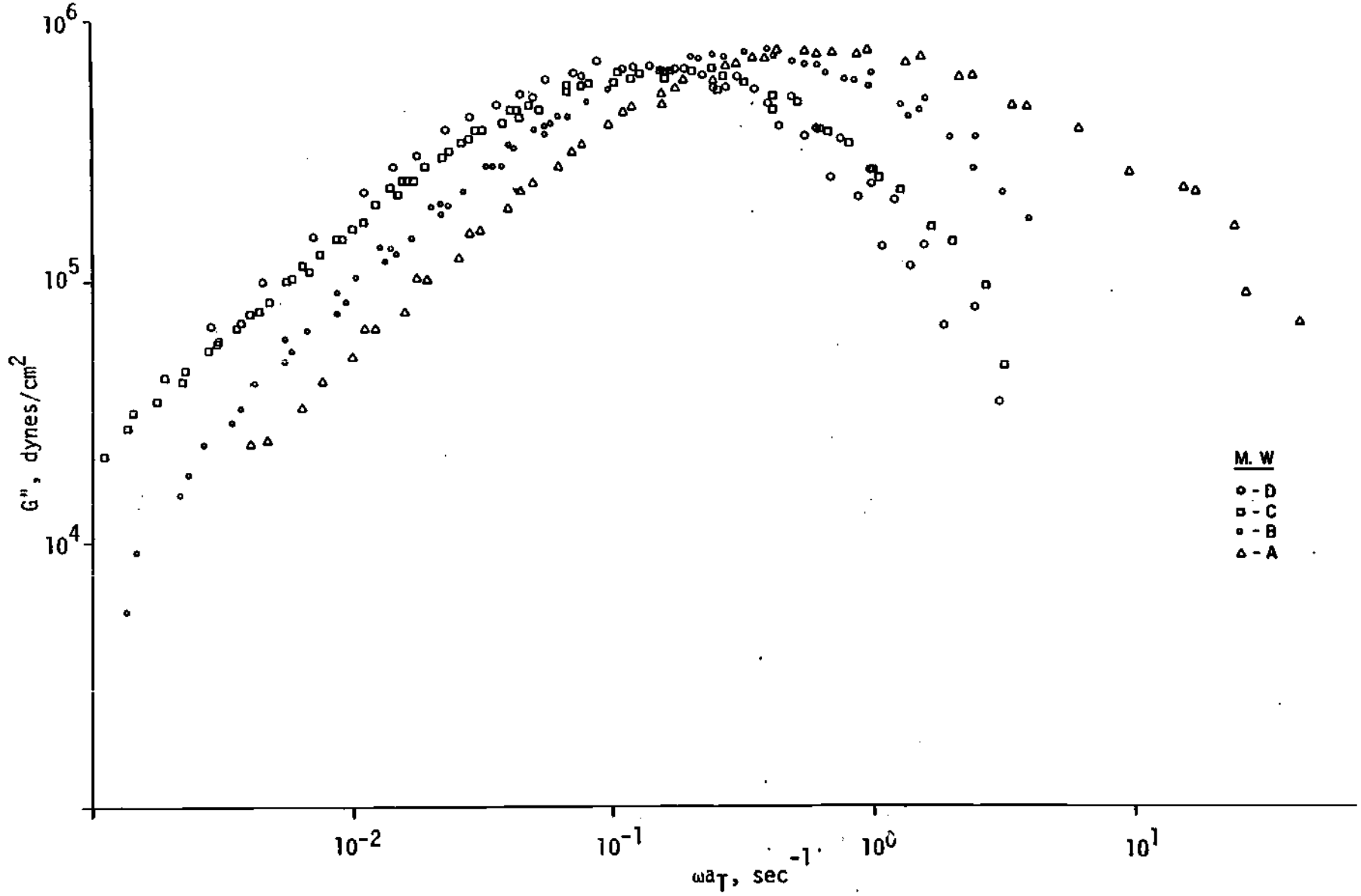


Figure 6. Loss Modulus Master Curves vs. Reduced Frequency at Reference Temperature, T_0= 473^{0}K

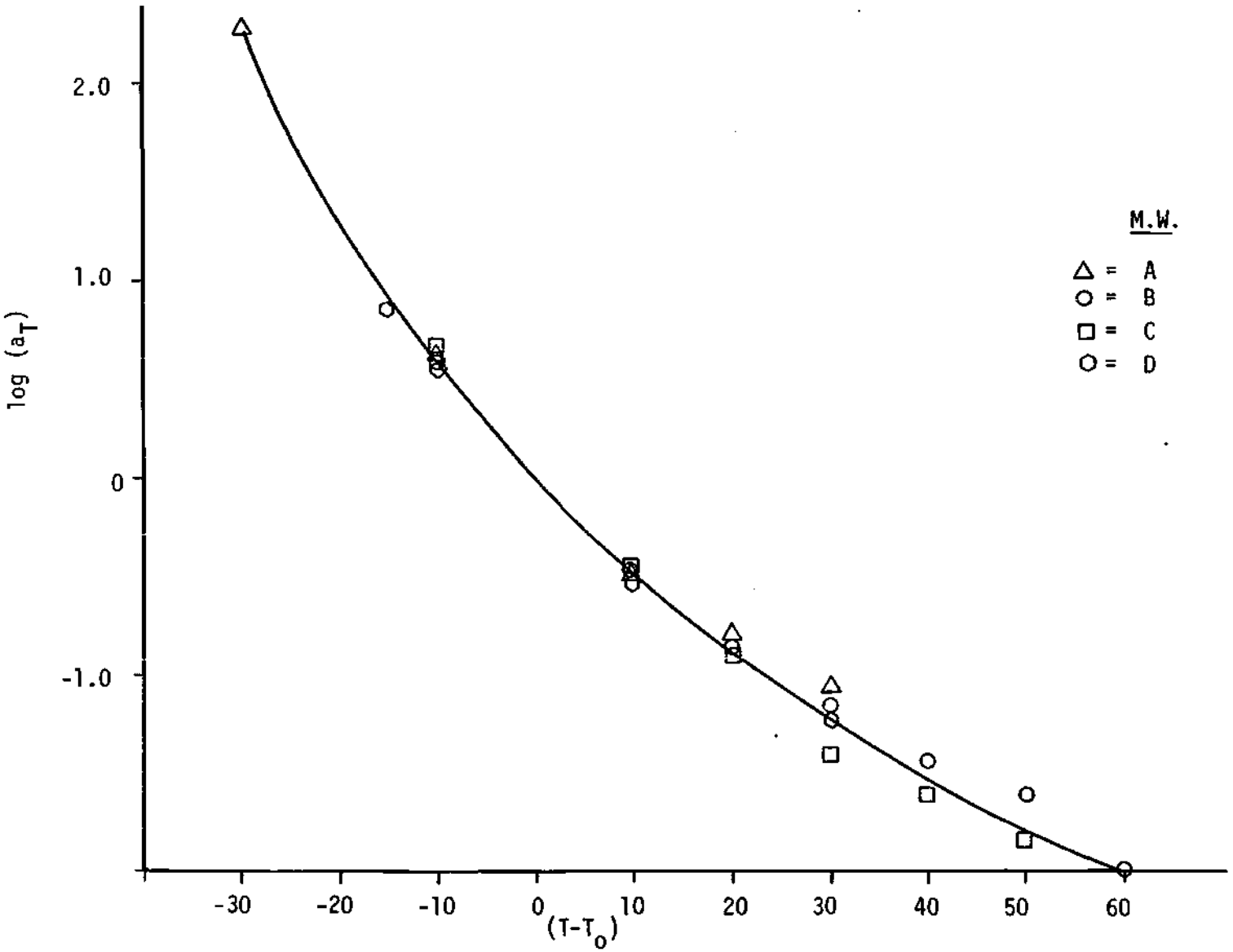


Figure 7. Shift Factor (a_T) vs. $T-T_o$

and had the values 5.23 and 98.4, respectively, for T_o=473^{o}K. The WLF equation is normally given in the following form:

$$\log a_T = \frac{C_1^o(T-T_o)}{C_2^o+(T-T_o)} \quad (48)$$

The least squares fit was based on 1/y versus X(where y is log a_T and x is $T-T_o$) and the fit factor r^2 was 0.979, a good fit.

Onogi, et.al characterized polystyrene samples of varying molecular weights for dynamic modulus and found that the shift factors were very close for the differing molecular weights.(9)

Coefficients C_1^g, and C_2^g were calculated for comparison purposes at the glass transition temperature of polycarbonate which is 150^{o}C. These coefficients may be calculated using the following equations:

$$C_1^g = \frac{C_1^o C_2^o}{(C_2^o+T_g-T_o)} \quad (49)$$

$$C_2^g = C_2^o+T_g-T_o \quad (50)$$

Having obtained these coefficients, other properties such as fractional free volume and thermal expansion of free volume may be calculated by comparison of WLF coefficients with those of the Doolittle equation for viscosity(12) which is given by:

$$\ln\eta=\ln A + B\,(1/f_g-1) \quad (51)$$

where A and B are empirical constants, the latter on the order of unity. The fractional free volume is given by:

$$f_g/B = \frac{1}{2.303\ C_1^g} \quad (52)$$

The thermal expansion coefficient is calculated according to the relation

$$\frac{\alpha_f}{B} = \frac{1}{2.303 C_1^g C_2^g} \tag{53}$$

and is a measure of the thermal expansion of free volume relative to the total volume at a reference temperature, T_g.

All coefficients were calculated at the glass transition temperature in order to make comparisons with the "universal" values. Experimental values for fractional free volume, thermal expansion coefficient of free volume and WLF constants are compared in Table 2 to the "universal" constants given in Ferry.[13] Universal values were obtained by fitting data on a large number of polymers and calculating average values of C_1^g and C_2^g from which f_g and α_f were determined. From the comparison made in Table 2, it is apparent that the experimental fractional free volume coefficient is somewhat larger than the universal value.

The experimental value of the thermal expansion coefficient also exhibits variation from the universal value. This coefficient as calculated in equation (53) is affected in a similar manner by the same factors which affect the free volume coefficient. It, too, is strongly affected by factors which influence the glass transition temperature.

Such deviation of experimental values from the universally accepted values has also been found in other polymers. For example,[13] poly-a-methyl-styrene, T_g=172°C, has a free volume fraction f_g/B=0.032 and thermal expansion coefficient $\alpha_f/B = 6.4 \times 10^{-4} deg^{-1}$. Another example, although not as close to polycarbonate in glass transition temperature as poly-α-methyl styrene, is poly(methyl methacrylate) T_g=115°C which has a free volume fraction f_g/B=0.013 and a thermal expansion coefficient $\alpha_f/B = 1.7 \times 10^{-4} deg^{-1}$. This

Table 2. Comparison of Universal Constants with Experimentally Determined Constants

Constants	Experimental	"Universal"
c_1^g	10.6	17.44
c_2^g	48.4	51.6
α_f/B	8.4×10^{-4}	4.8×10^{-4}
f_g/B	0.0409	0.025

information is compiled in Table 3 for comparison purposes. Both polymers in the examples are substantially different in their chemical structure from polycarbonate and both show variation from the universal values for free volume fraction and thermal expansion coefficient. Polymer structure (i.e., branched or straight chain) and number average molecular weight strongly influence the glass transition temperature and with it the fractional free volume and its thermal expansion coefficient.

2. Dynamic Viscosity

Experimentally determined values of loss and storage moduli as a function of frequency were used to calculate complex dynamic viscosity, η^*, as a function of frequency using Equation (35) which was developed in the theory section. Plots of η^* versus ω are shown in Figures (C-1)-(C-4) in Appendix C.

Master curves for each molecular weight were constructed at a reference temperature T_o=200°C from dynamic viscosity versus frequency isotherms using Equation (41), which was derived in the theory section to be:

$$\eta^*(\omega,T)=a_T\eta^*(\omega a_T,T_o) \qquad (41)$$

The curves for each molecular weight are shown in Figure 8 and exhibit minimal data scatter.

As discussed in the previous section, G' and G" shifted graphically with respect to the frequency abscissa. The above equation requires that the dynamic viscosity shift vertically, that is with respect to the log viscosity ordinate, and horizontally, which means with respect to the log frequency abscissa, by equal amounts. Furthermore, the vertical and horizontal shifts may be made analytically and will both be based on a_T (which had been determined in the graphical shifting of moduli isotherms into master curves). All four molecular

Table 3. Comparison of Universal Constants with Experimentally Determined Values for Various Polymers

POLYMERS	T_g(°C)	$\alpha_{f/B}(deg^{-1})$	$f_{g/B}$
poly-α-methyl styrene	172	6.4×10^{-4}	0.032
Poly (methyl methacrylate)	115	1.7×10^{-4}	0.013
polycarbonate	150	8.4×10^{-4}	0.041
universal values	-	4.8×10^{-4}	0.025

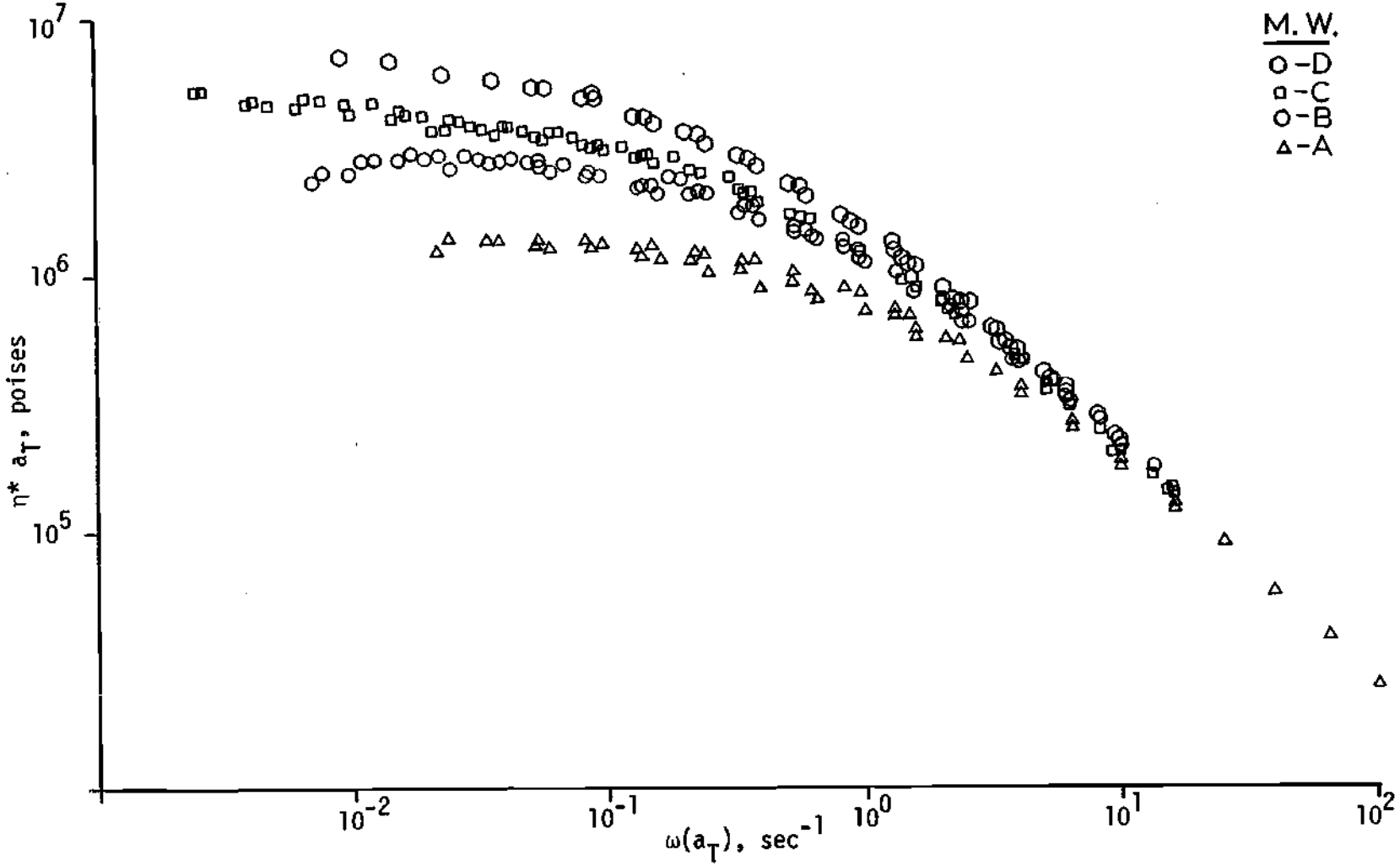


Figure 8. Complex, Dynamic Viscosity Master Curves vs. Reduced Frequency at Reference Temperature, T_o=473K.

weights were shifted by the same a_T function used in shifting the moduli data graphically in the last section.

Time-temperature superposition of the real part, η', of the complex dynamic viscosity has been dealt with in the literature more than has superposition of η^*. Ferry developed a method for shifting the real part of the dynamic viscosity using an array of Maxwell elements in parallel that assumed that the relaxation mechanisms, which contribute to G' and η_j^* would have the same temperature dependence so that when changing from a standard temperature to another temperature each relaxation mechanism would be multiplied by the same a_T.[14]

That a_T, obtained in shifting moduli isotherms into master curves, should be the same used to shift complex dynamic viscosity is not well recognized in the literature. Onogi, et.al., working with polystyrene observed that for a given material, the shift factors a_T obtained in shifting η^* and G' were practically the same.[9] In fact, the mathematical relationship required that the shift factors be the same.

The magnitude of the complex dynamic viscosity has been found by many investigators to be quite closely related to flow properties for many polymers. It is reasonable to assume that dynamic viscosity, η^*, and apparent viscosity, η_a are related, since dynamic viscosity is the oscillatory response analog of the steady flow viscosity. The assumption which must be made is that frequency and shear rate are directly comparable. Strella[15] showed mathematically that shear rate is equal to frequency for a Kelvin element. There is disagreement among investigators, however, as to how closely the dynamic and apparent viscosities are related when making experimental

comparisons. Attempts to compare dynamic viscosities from this investigation with apparent viscosities of the same materials obtained on a Sieglaff-McKelvey Rheometer were not successful. Efforts to locate literature comparing dynamic and steady flow capillary viscosities of polycarbonate have been fruitless. Several investigators have found correlation between dynamic and apparent viscosities. Mendelson, et.al., found excellent correlation between dynamic and capillary steady shear data on polyethylene.[16] Cox and Merz also found good correlation in experiments on polystyrene comparing apparent viscosity with dynamic viscosity.[17] Working with polypropylene, Adamse, et.al., found good agreement between dynamic and steady shear data.[18] Still other investigators have found good correlation with some polymers and poor correlation with others. For example, Ferry found rather good correlation with polystyrene and very poor correlation with polyvinyl acetate.[19] This led Ferry to suggest that a wide spread of molecular weights, that is a high molecular weight distribution and branching in the samples may account for the lack of correlation with the polyvinyl acetate. Ballman and Simon compared η^* and η_a in monodispersed polystyrene experiments and found poor agreement.[20] This is certainly not due to a large molecular weight distribution. The polymer may possibly have branching, but it is mere speculation that this may cause the lack of correlation. Apparent viscosity, η_a, unlike the complex dynamic viscosity, η^*, is not constrained to linear viscoelasticity. Consequently, η^* and η_a need not necessarily be related.

B. Molecular Weight Superposition

1. Dynamic Shear Modulus

The master curves obtained for G' and G" as a function of frequency at a reference temperature, T_0, may be further reduced to a reference molecular weight. Shift formulae were developed in the theory section for reducing

loss and storage moduli to a reference molecular weight as follows:

$$G'(\omega,T,M) = = G'(\omega a_T a_M, T_o, M_o) \tag{24}$$

$$G''(\omega T,M) = G''(\omega a_T a_M, T_o, M_o) \tag{25}$$

The master curves of G' vs. ωa_T and G" vs. ωa_T were shifted graphically by a_M into master curves at a reference weight average molecular weight of 32,400, designated M_o. Only a horizontal shift was required to obtain the master curves shown in Figures 9 and 10.

A plot of log a_M Vs. log $(\overline{M}_w)$ is given in Figure 11, which was obtained by fitting the data to a linear regression of a least squares plot of the equation:

$$a_M = K(\overline{M}_w)^b \tag{54}$$

A least squares fit factor (defined as correlation coefficient) in this investigation was found to be $r^2 = 0.998$ which is indicative of a rather good data fit to the equation. From the linear regression, the slope was determined to be 3.83. Having obtained these coefficients the loss and moduli curves can be shifted to any other reference molecular weight where dynamic moduli properties are desired over a broad frequency range. The master curves are also quite useful as a quality control tool. For example, if polycarbonate of known molecular weight is suspected of degradation during processing, an isotherm of the processed material may be run and compared to the master moduli curves. If the molecular weight has changed the isotherm will not overlay the master curve well, but rather will be of slightly differing shape.

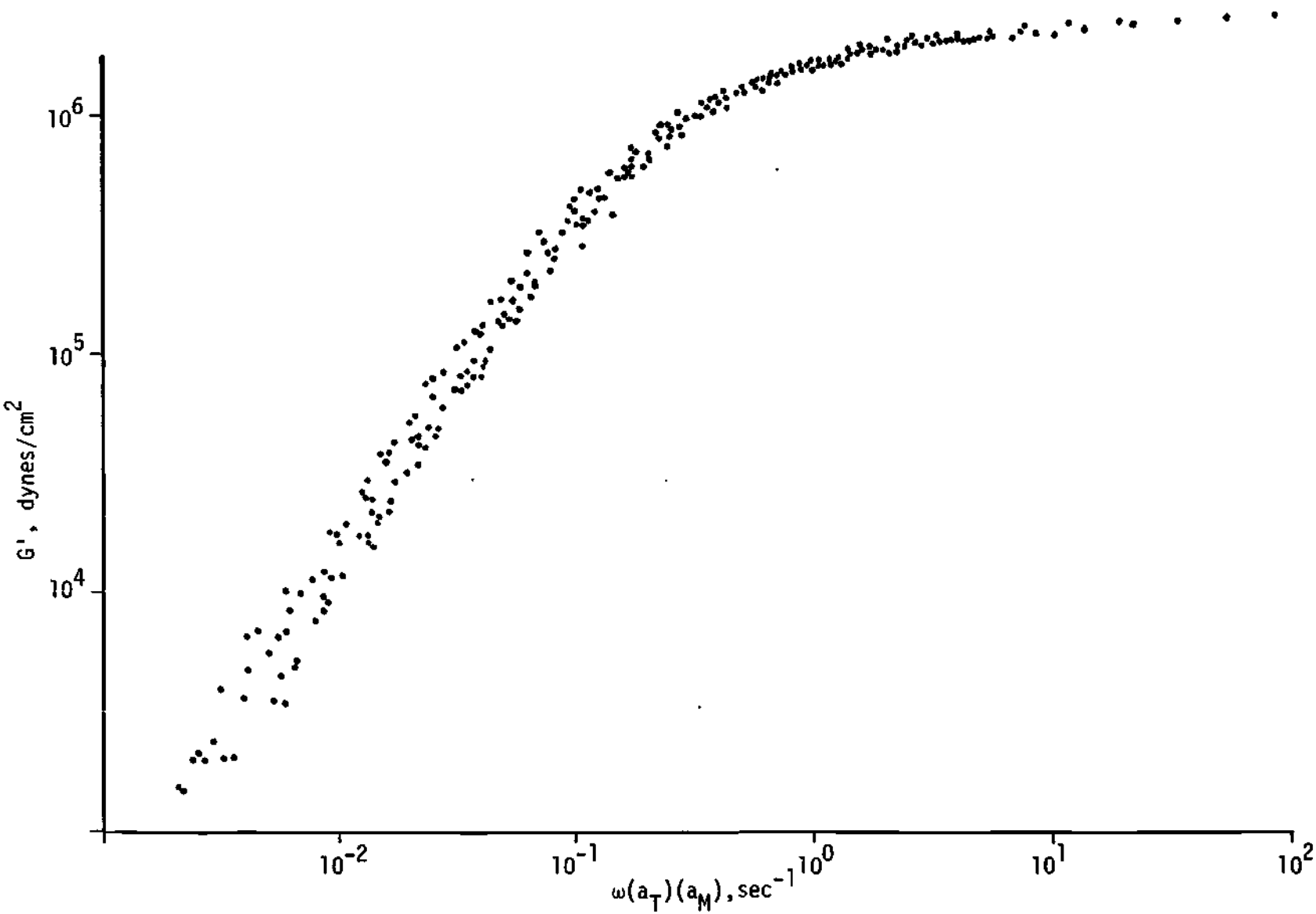


Figure 9. Storage Modulus Master Curve vs. Reduced Frequency at Reference Temperature, T_o=473K and Reference Molecular Weight B , M_o=32,400

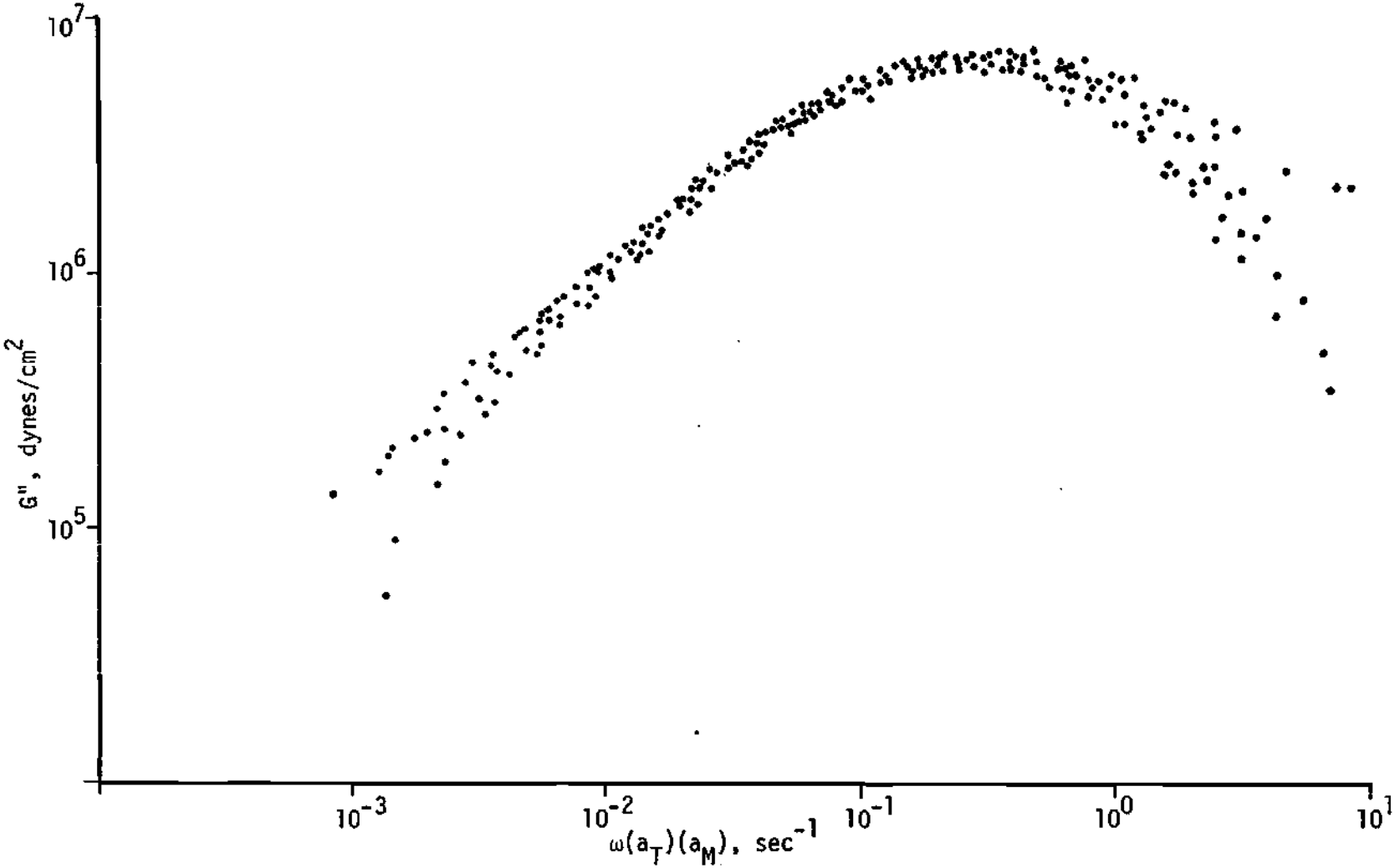


Figure 10. Loss Modulus Master Curve vs. Reduced Frequency at Reference Temperature, T_o=473K and Reference Molecular Weight B , M_o=32,400

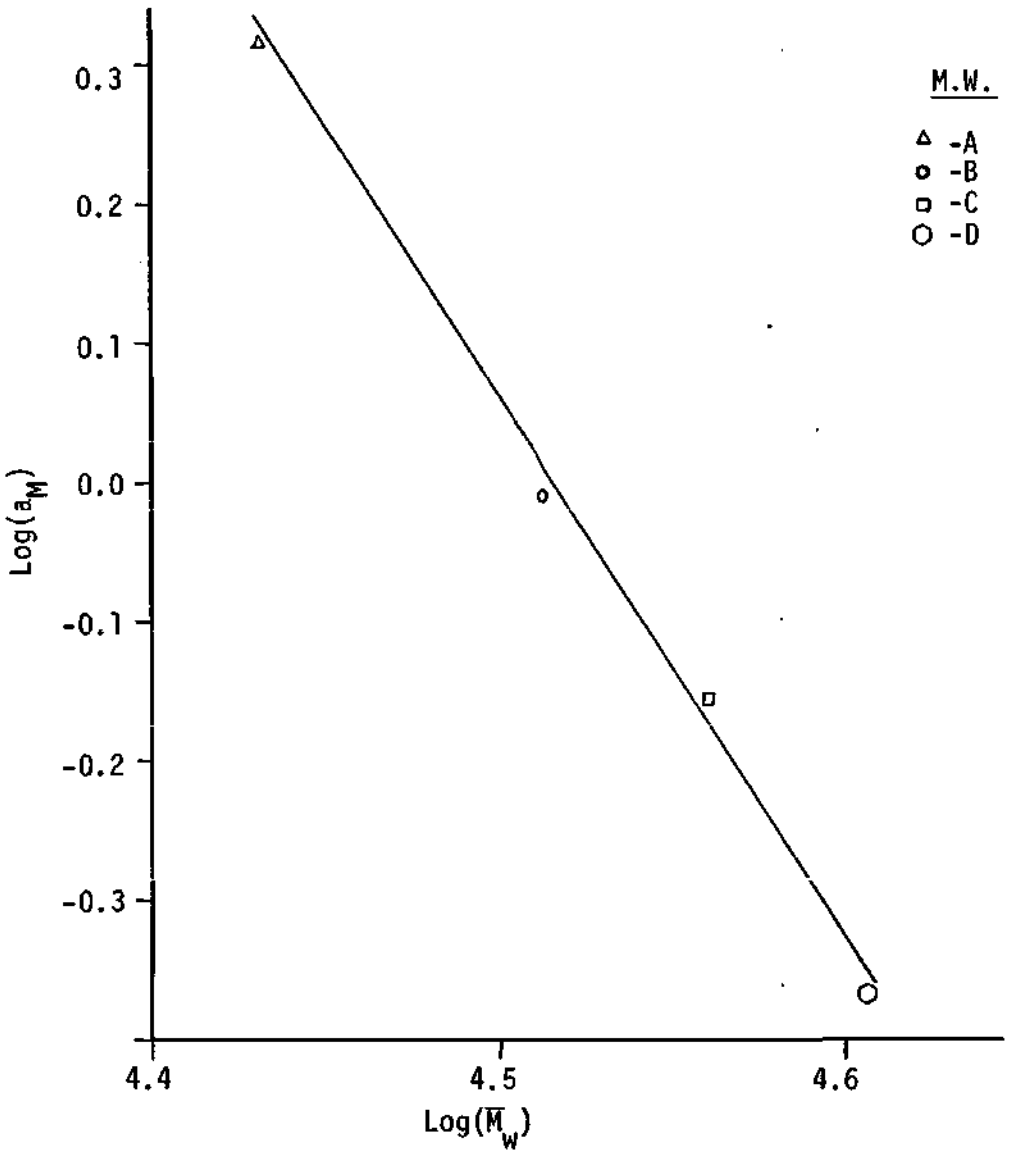


Figure 11. Molecular Weight Shift Factor (a_M) vs. Weight Average Molecular Weight.

2. Dynamic Viscosity

Using shift formulae developed in the theory section, it is possible to shift viscosity master curves at a reference temperature T_o, to a reference molecular weight as follows:

$$\eta^*(\omega,T,M) = a_T a_M \eta^* \quad (\omega a_T a_M, T_o, M_o) \tag{42}$$

The formulae require that a vertical and horizontal shift (i.e. shifts with respect to the log frequency abscissa and log viscosity ordinate), both equal in magnitude to log a_M, be made to shift viscosity curves to a reference molecular weight. Further, the shifts can be made analytically using a_M obtained in the graphical shifting of loss and storage moduli to reference molecular weight, M_o. The viscosity master curve at reference weight average molecular weight M_o=32,400 and reference temperature T_o=200°C is shown in Figure 12. The curves came together very nicely with hardly any data scatter.

Having such a master curve for dynamic viscosity or dynamic moduli will allow shifting of the master curve itself to any other molecular weight using equation (54). This then permits prediction of dynamic viscosity or dynamic moduli over a broad frequency range for virtually any molecular weight of polycarbonate, provided the chemical structure is not significantly different. It has been found in the literature that most polymer systems follow an equation similar to equation (55) relating viscosity and molecular weights as follows:

$$\eta_o = K(\overline{M}_w)^b \tag{55}$$

where b equals 3.5 $\pm$ 0.5 above the critical molecular weight.[2] From a logarithmic plot of η_o vs. $(\overline{M}_w)$, b was found to have a value of 4.12. Since a_M is a molecular weight viscosity function, equations (54) and (55) should be identical, with identical slopes. Experimental error most likely accounts

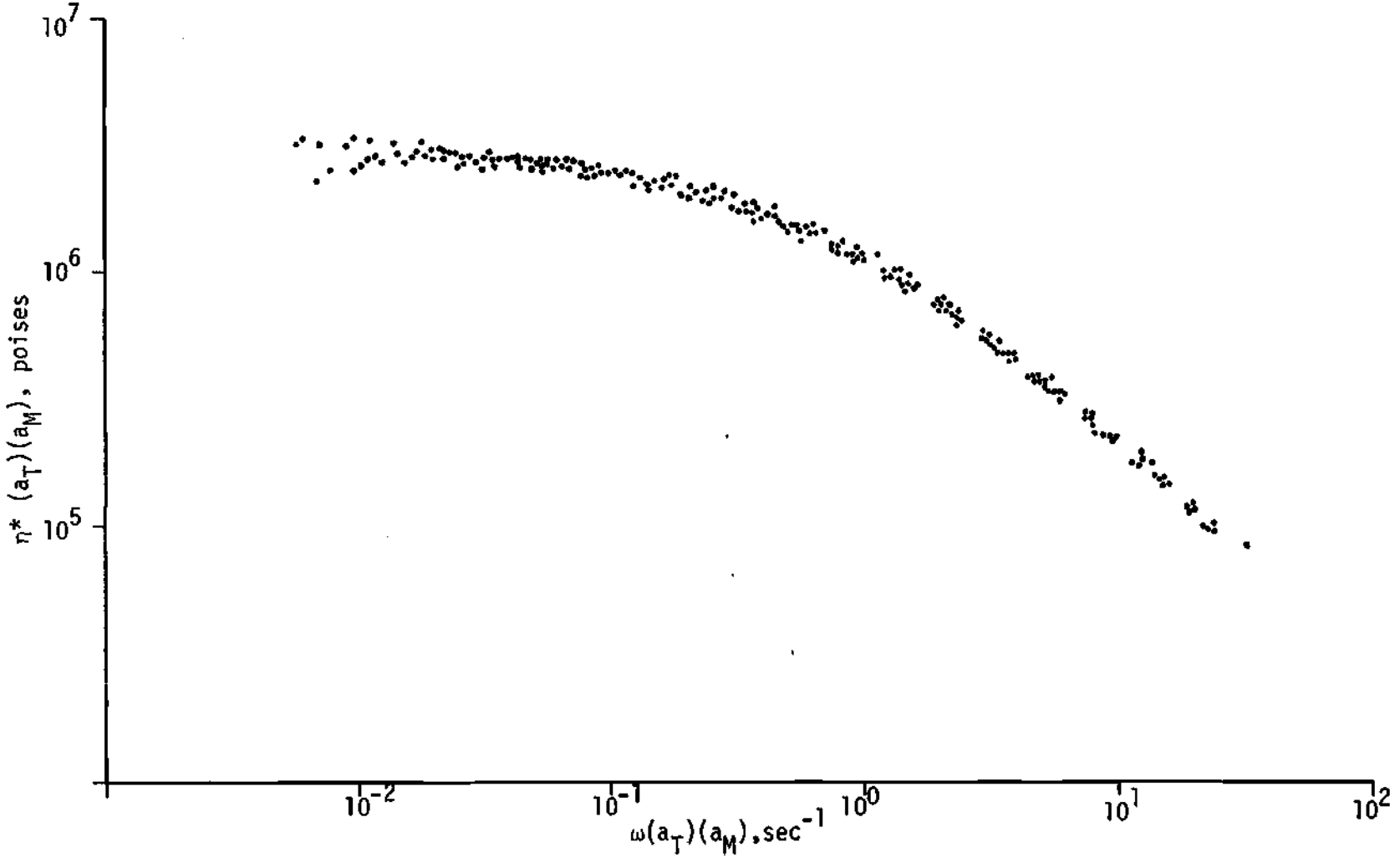


Figure 12. Complex, Dynamic Viscosity Master Curve vs. Reduced Frequency at Reference Temperature, T_o=473K and Reference Molecular Weight B, M_o=32,400

for the difference between a b value of 3.83 from equation (54) and 4.12 using equation (55). The average of these two is 3.98 ± 0.14 which would undoubtably shift my data nicely.

The approach used to shift data in this investigation did not make use of a model, rather it required that the material satisfy a constraint of linear viscoelasticity. Several investigators have worked in the area of shifting viscosity curves to reference molecular weights. Ballman and Simon[20] working with monodispersed polystyrene utilized a model developed by Bueche[21], Harding and Rouse[22] to obtain a reduced apparent viscosity (η_a/η_o) versus shear rate ($\dot{\gamma}\lambda_1$) plot. The longest or terminal relaxation time, λ_1, is given by:

$$\lambda_1 = \frac{12\eta_o M}{\pi^2 RT} \qquad (56)$$

and dominates the properties in the terminal zone of the frequency scale.[2] The terminal relaxation time is a measure of the time required during annealing for internal stresses to relax. It is also a measure of the time required to reach a state of steady flow under constant stress versus the time required for elastic recoil after the stress is removed. In undiluted systems of molecular weights below approximately 20,000, molecular motions and configurational changes are much the same as in diluted systems if coupling entanglements do not occur.[2] The primary effect in going from a system where solvent molecules are in the matrix to a system where polymer molecules alone are present is to increase the relaxation times, all by the same factor. Rouse's theory (or Bueche's theory) has its basis in the free energy change associated with the decrease in entropy for non-random configurations and the tendency of the system to approach a random state. Energy stored and dissipated

in sinusoidally oscillating deformations may be calculated from this theory.

Ballman and Simon found that employing λ_1 to shift their data resulted in the horizontal and vertical shifts not being equal. The vertical shift will be equal to η_o which is related to molecular weight by a power b. The horizontal shift factor, λ_1, is proportional to the molecular weight by a power b+1, which is not linear. The reduction procedure of Ballman and Simon apparently works, but since it does not satisfy my shift criteria that horizontal and vertical shifts be equal, it may be outside the bounds where my mathematical relationships hold.

Stratton experimentally shifted apparent viscosity (η_a) temperature master curves of narrow distribution polystyrene by vertical and horizontal shift factors which he denotes a_V and a_h.[23] A close examination of his plots of a_h and a_V as a function of weight average molecular weight reveals that $a_h=a_V$. This reduction procedure begins to approach the procedures used in my investigations. Stratton recognized the shortcomings of the Bueche-Harding procedure for constructing master curves at reference temperature and molecular weight. He refined the apparent viscosity work of Ballman and Simon by introducing the molecular weight term to a power; thus, changing the terminal relaxation time, λ_1, as follows:

$$\lambda_1 = \frac{\eta_o (\bar{M}_w)^{\frac{-\alpha(1+\beta)}{\beta}}}{\rho RT} \qquad (57)$$

He defined α to be equal to the slope of the log η_o vs. log $(\bar{M}_w)$ curve which was 3.34. β was defined as the slope of the line connecting the terminal viscosity plots of various molecular weights in a logarithmic graph of viscosity versus shear rate (i.e., β is equal to $\frac{\log a_V}{\log a_h}$), and the slope was found to be -0.82. The slope of the log a_h versus log $(\bar{M}_w)$ he defined as α/β and found to be -4.10. After reducing the data of Ballman and Simon

according to the modified Bueche procedure, he obtained a much better master curve than they had gotten in their original reduction according to Bueche. Substituting equation (55) (and substituting α for b) in equation (57) results in:

$$\lambda_1 = \frac{K\bar{M}_w}{\rho RT}^{-\alpha/\beta} \qquad (58)$$

In this investigation I found α equal to 4.12 and $\alpha/\beta = 3.83$. From this, β may be calculated and equal 1.07. The constants, found in this investigation, are very close to those found by Stratton. Since β is equal to $\frac{\log a_V}{\log a_b}$ then Stratton's analysis also supports equation (55). The investigation of Stratton is in clear agreement with the data and analysis of the investigation presented here.

Mendelson[24] et.al., followed the Bueche-Harding procedure and found that it was insufficient to reduce apparent viscosity data on several molecular weights of polydisperse high density polyethylene to a single curve at a reference molecular weight and temperature. In order to reduce the data to a single master curve they introduced a shift factor χ_M equal to:

$$\chi_M = \left(\frac{1}{\dot{\gamma} \lambda_1} \right)^{0.53} \qquad (59)$$

where λ_1 is the terminal relaxation time described by Bueche. This means that the curves were forced to superpose at $\lambda\dot{\gamma}_1 = 1$ which is the point at which $\eta_a/\eta_o = 0.53$. The horizontal and vertical shifts are very close to the same, in agreement with the results presented here.

Hwo and Johnson applied Bueche's procedure of reduced variables to apparent viscosity (η_a) flow curves of polydispersed polyvinyl chloride polymers of widely varying molecular weights. Data scatter was substantial as might be expected since many have reported on the failure of the Bueche

models working alone in polydispersed polymeric systems.

The polydispersity (M_w/M_n) for the polymers used in Hwo and Johnson's study was between 2.03 - 2.89 which is a somewhat broader spread of distributions than those used in this investigation (2.30-2.58).

The only comparison made between complex dynamic viscosity data in this investigation and that of other investigations was taken from the work of Ballman and Simon,[20] who shifted dynamic viscosity (η') versus frequency isotherms of monodispersed polystyrene into master curves using the Bueche-Harding model described earlier. They found that this procedure gave them very good master curves for monodisperse systems (M_w/M_n)<1.1), but yielded very poor master curves for polydisperse systems (M_w/M_n=3.02-3.40). This model as described earlier does not approach my shift criteria, and is probably outside the bounds of my mathematical relationships.

Several of these investigators used models which (although my shifting requires a linear viscoelastic constraint and not a model) approached my shift criteria and worked for constructing good master curves. Others used models which did not approach my shift criteria but worked nonetheless. These models are most likely operative outside the bounds of my mathematical relationships.

The usefulness of the viscosity curves, aside from any comparison with flow properties, is as a quality control tool. Once master curves have been generated for these four molecular weights a basic shape for the curve has been established. Having these master curves allows one to run an isotherm of dynamic viscosity versus frequency for a polycarbonate of unknown molecular weight and extrapolate the remainder of the curve on the basis of the shape of the other master curves. From this, predictions of dynamic viscosity can

be made over a broad range of frequency from a single isotherm, and predictions can also be made on the magnitude of the molecular weight.

CHAPTER V

CONCLUSIONS

1. Polycarbonate of bisphenol-A is linearly viscoelastic in eccentric, oscillatory shear at strains up to 5 percent in the 0.1 to 10^2 cycles per second frequency range.
2. The components of the complex shear modulus (loss and storage moduli) shifted to a reference temperature and reference molecular weight by graphical logarithmic shifts along the frequency abscissa.
3. Loss and storage moduli were shifted by the same shift factors.
4. The temperature-frequency relationships for the plateau and terminal zones of the complex shear modulus were described well by the WLF equation and were in reasonable agreement with published data.
5. The complex dynamic modulus was analytically shifted into master curves at reference temperature and molecular weight by equal logarithmic shifts with respect to the frequency abscissa and viscosity ordinate.
6. The shift factors, a_T and a_M, for shifting complex dynamic viscosity were obtained from graphically shifting complex moduli data logarithmically with respect to the frequency abscissa.
7. No correlation was found between apparent viscosity (η_a)(obtained from capillary flow experiments) and complex dynamic viscosity for polycarbonate in this investigation.
8. Shifting of dynamic viscosity curves to a reference temperature and a reference molecular weight resulted in good master curves having little scatter of data.

CHAPTER VI

RECOMMENDATIONS

1. Since many investigators have found correlation between dynamic and apparent viscosities for polymers other than polycarbonate various geometries should be investigated to determine if correlations can be made for polycarbonate.
2. Correlation between mechanical integrity and changes in complex dynamic moduli and viscosity should be investigated along with changes in molecular weight.
3. A correlation between molecular weight distribution changes and the shapes of dynamic moduli and viscosity curves should be developed.
4. The change in molecular weight distribution from the highest to the lowest molecular weight in this investigation was approximately 50%. The method by which a broader spread of polydispersities affects the data scattering when shifting dynamic properties should be investigated.

APPENDICES

APPENDIX A

Storage Modulus Versus Frequency Isotherms For Molecular Weights A-D

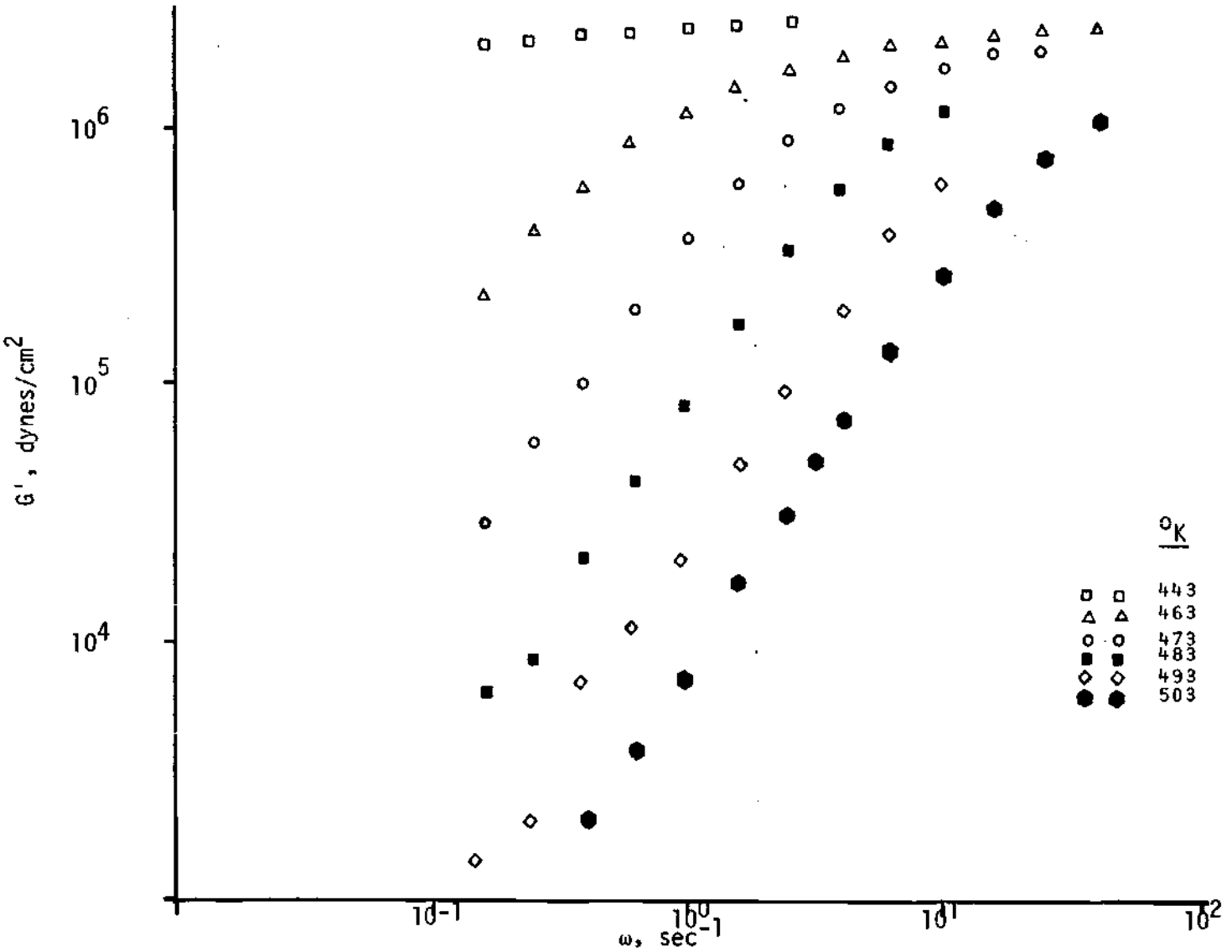


Figure A-1. Storage Modulus vs. Frequency for Molecular Weight A, ($\bar{M}_w$)=26,900

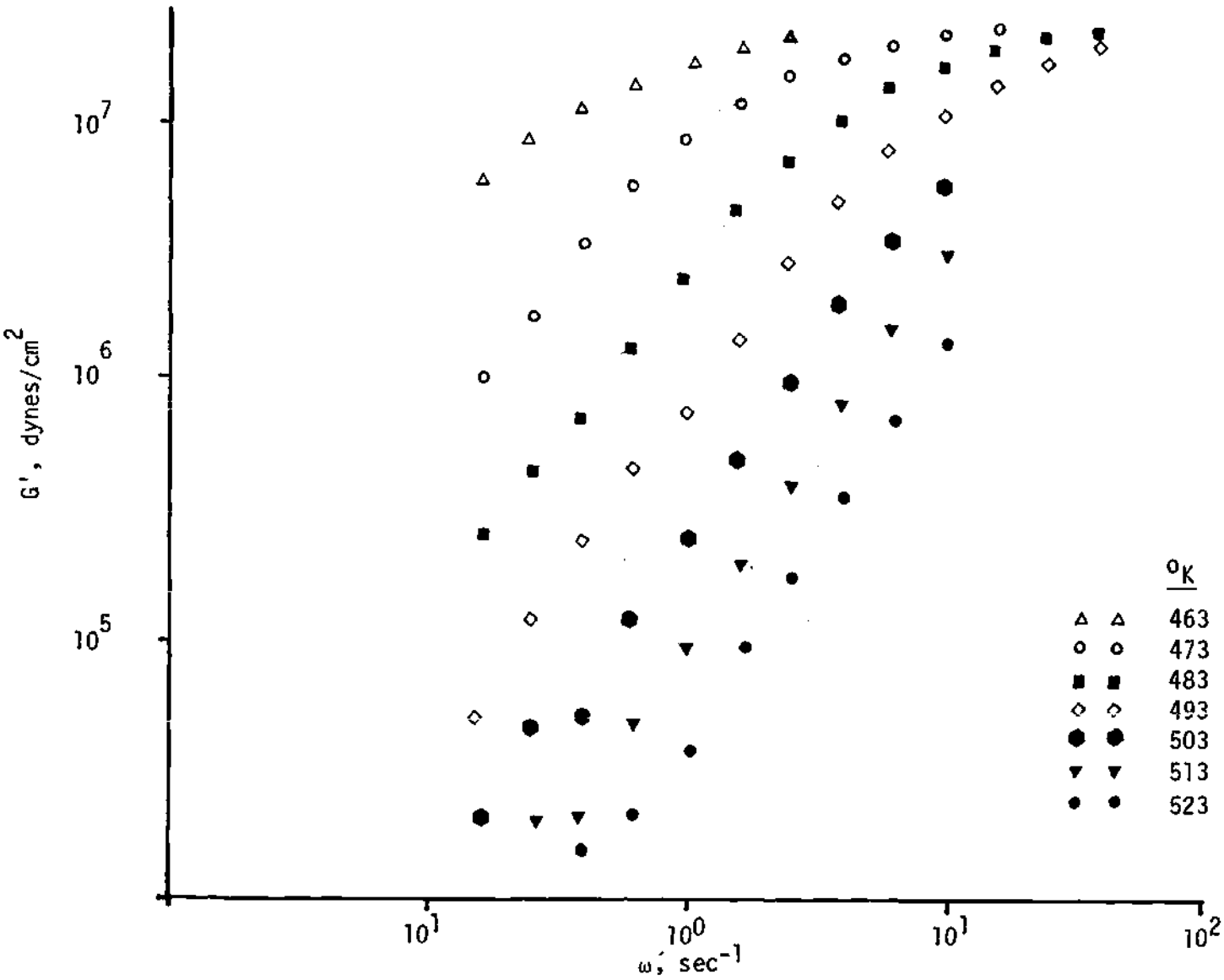


Figure A-2. Storage Modulus vs. Frequency for Molecular Weight B, ($\overline{Mw}$)=32,400

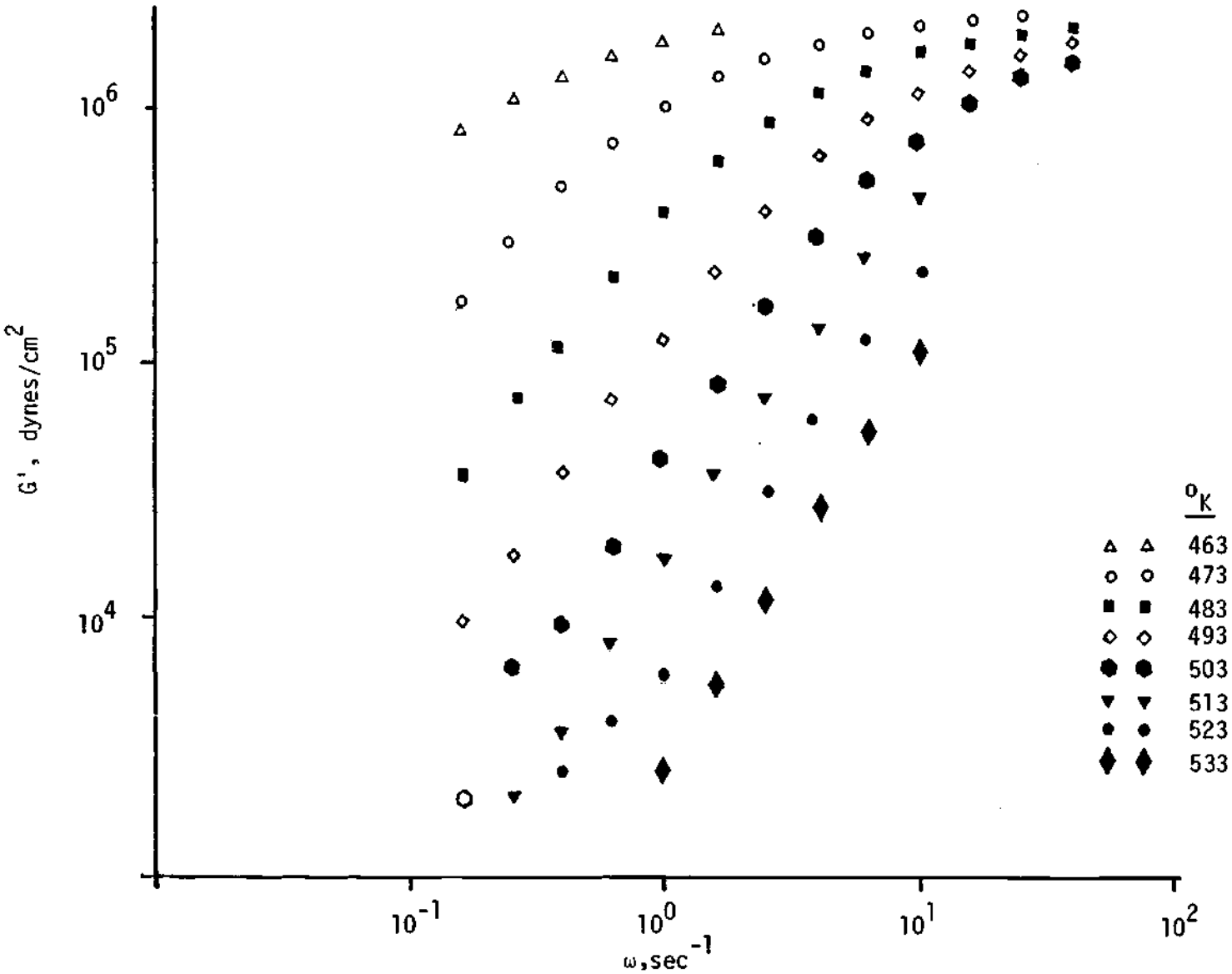


Figure A-3. Storage Modulus vs. Frequency for Molecular Weight C, ($\overline{M}_w$)=36,300

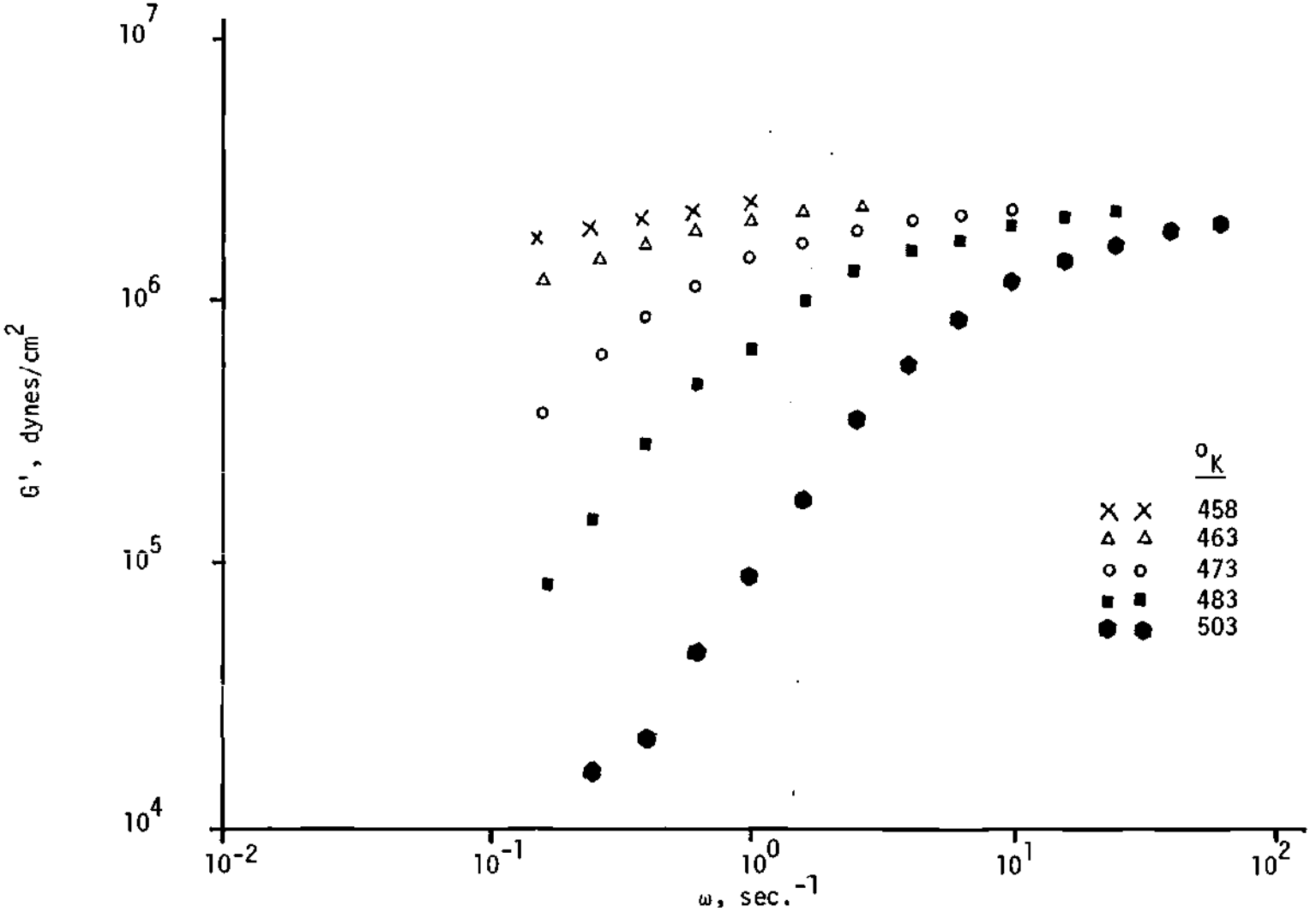


Figure A-4. Storage Modulus vs. Frequency for Molecular Weight D, ($\bar{M}_w$)=40,400

APPENDIX B

Loss Storage Versus Frequency Isotherms

For Molecular Weights A-D

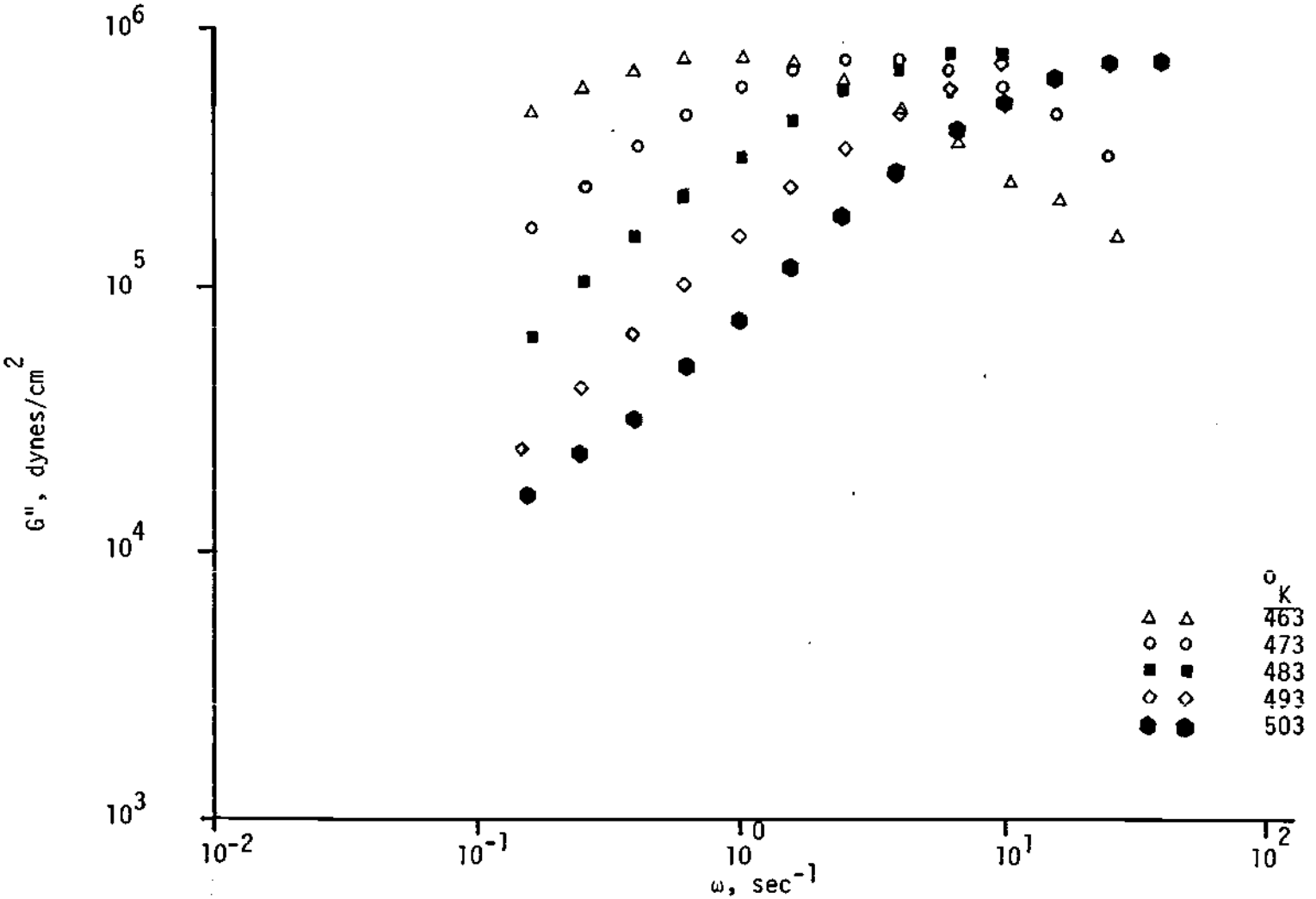


Figure B-1. Loss Modulus vs. Frequency for Molecular Weight A, ($\overline{M}_w$)=26,900

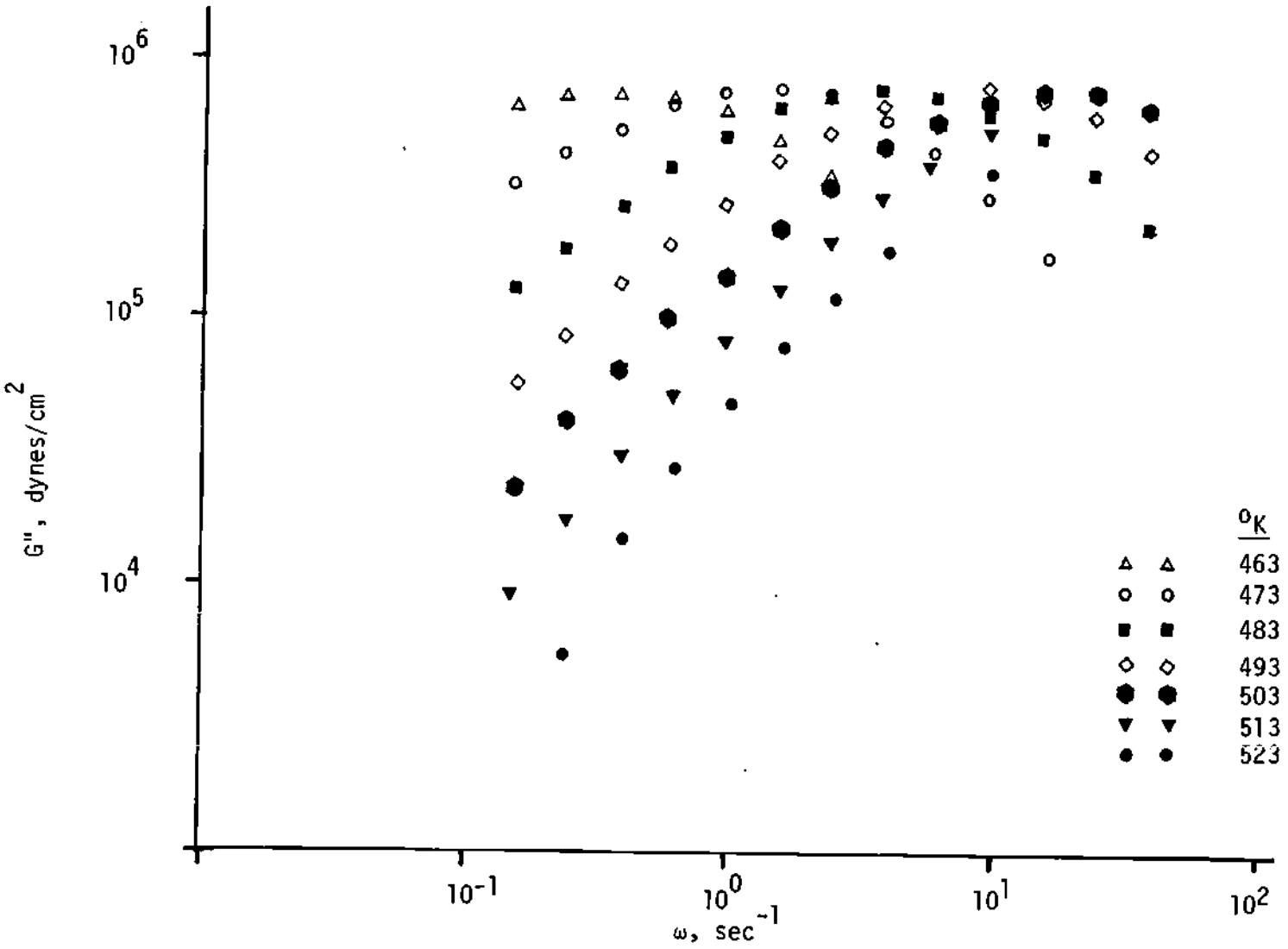


Figure B-2. Loss Modulus vs. Frequency for Molecular Weight B, ($\overline{M}_w$)=32,400

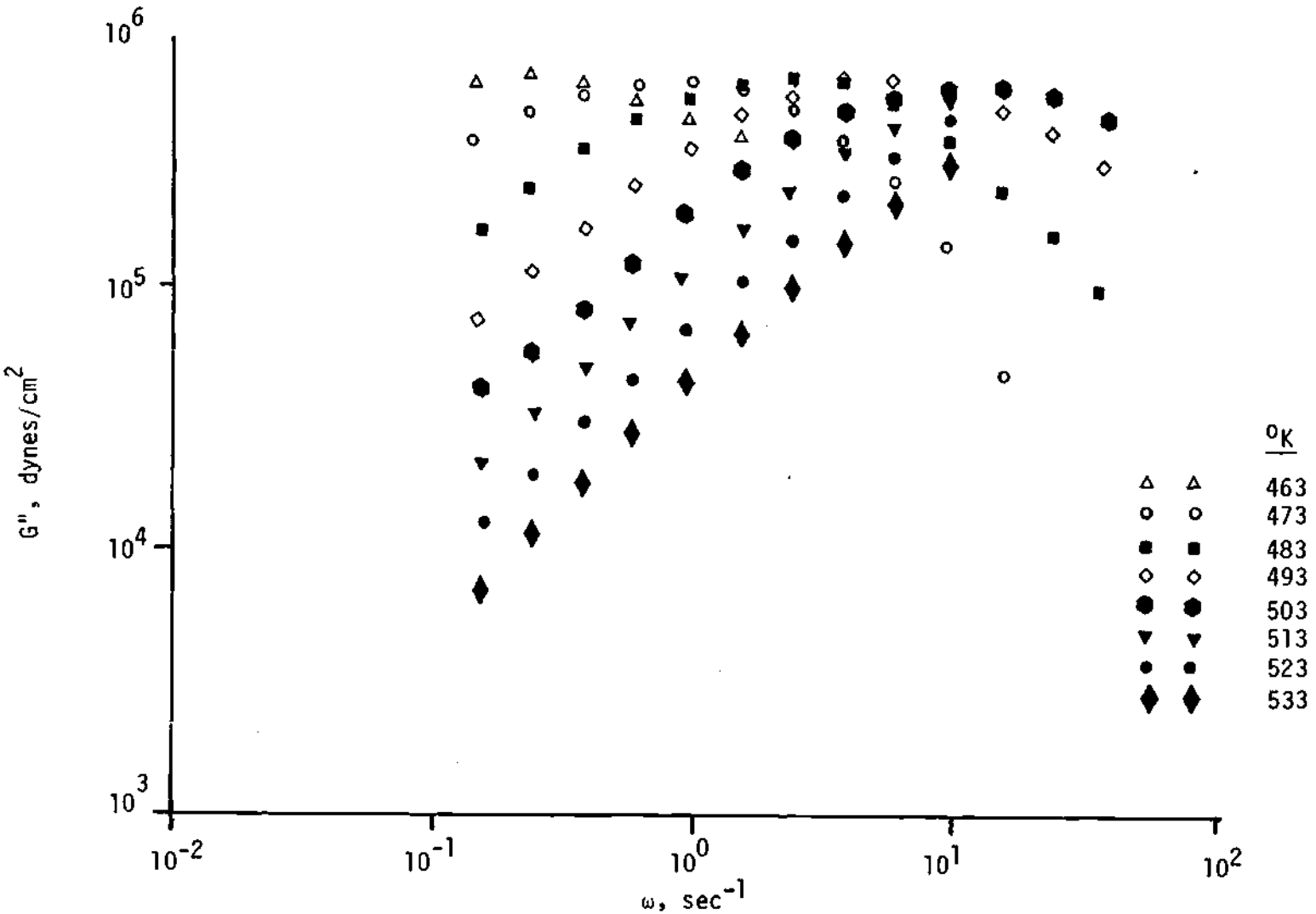


Figure B-3. Loss Modulus vs. Frequency for Molecular Weight C, ($\overline{M}_w$)=36,300

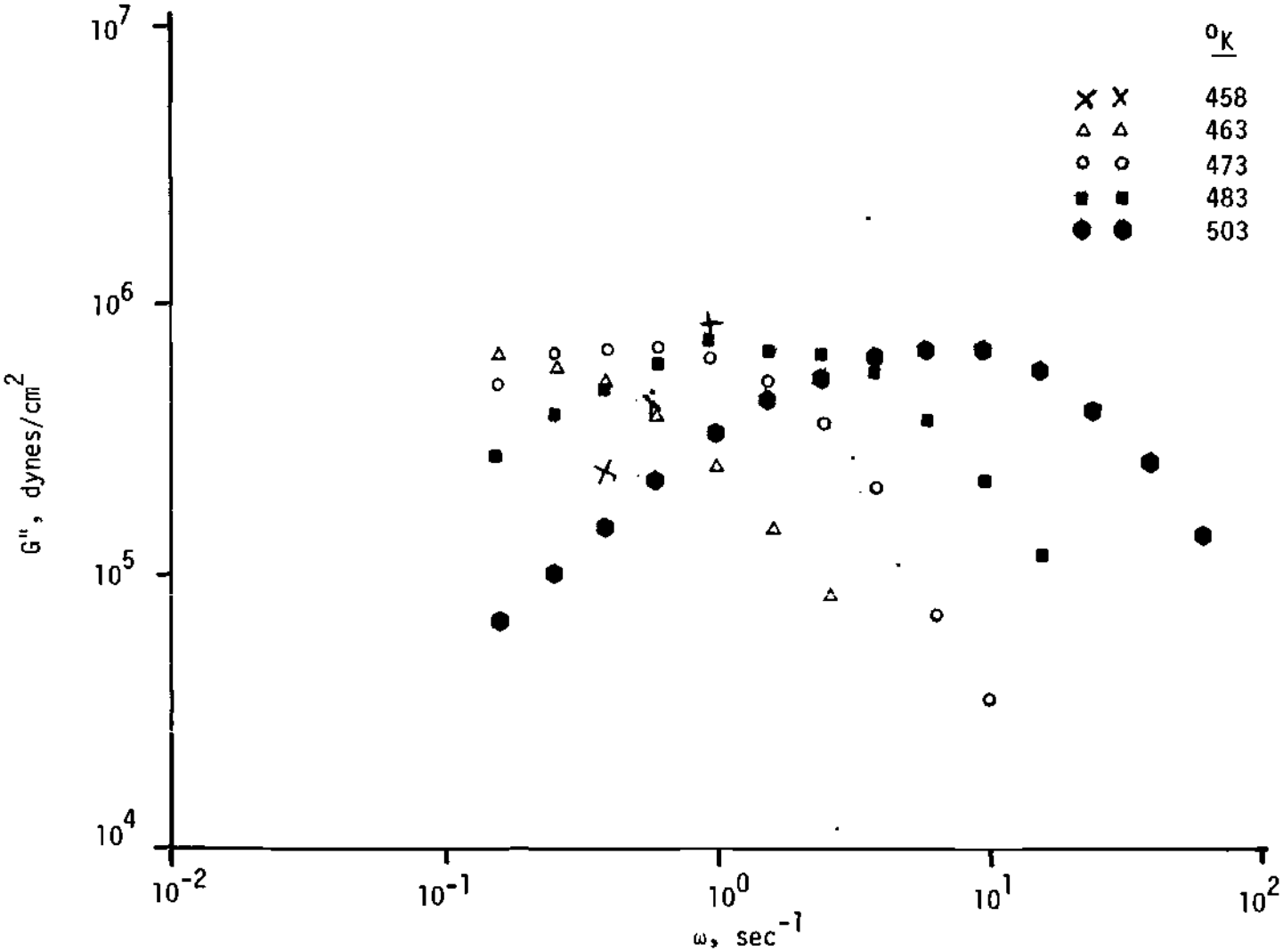


Figure B-4. Loss Modulus vs. Frequency for Molecular Weight D, ($\overline{M}_w$)=40,400

APPENDIX C

Dynamic Viscosity Versus Frequency Isotherms

Molecular Weights A-D

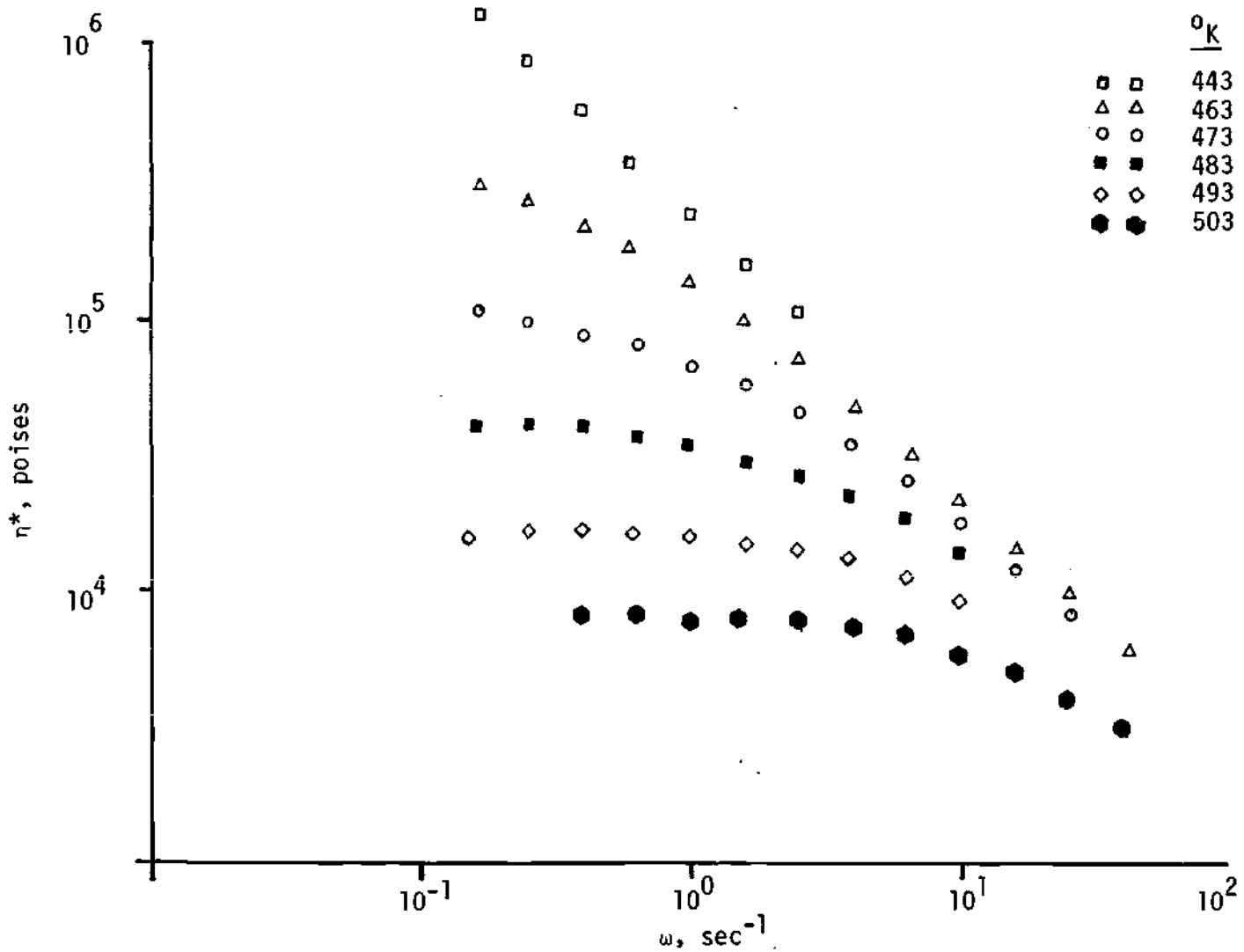


Figure C-1. Complex, Dynamic Viscosity vs. Frequency for Molecular Weight A, ($\bar{M}_w$)=26,900

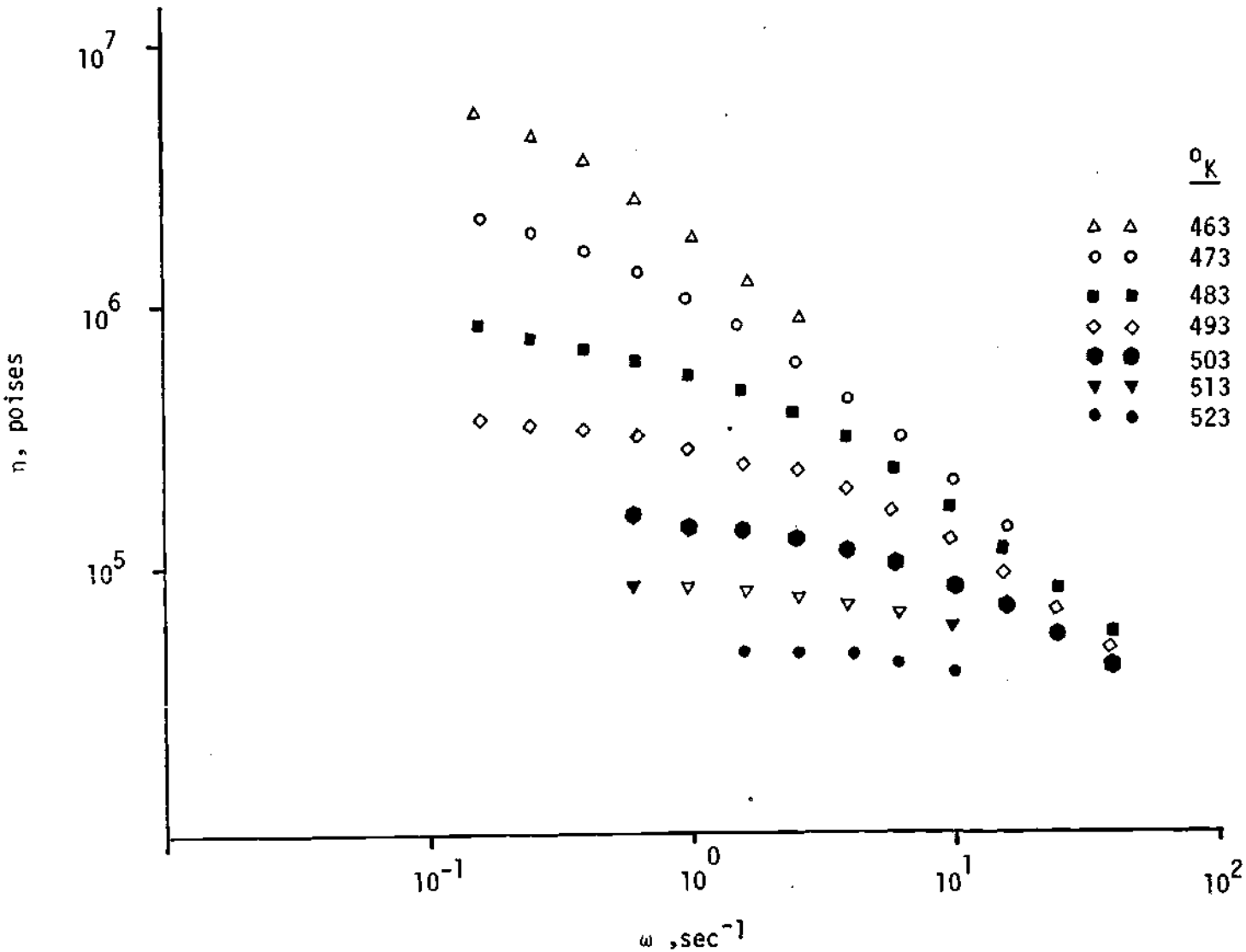


Figure C-2. Complex, Dynamic Viscosity vs. Frequency for Molecular Weight B, ($\overline{M}_w$)=32,400

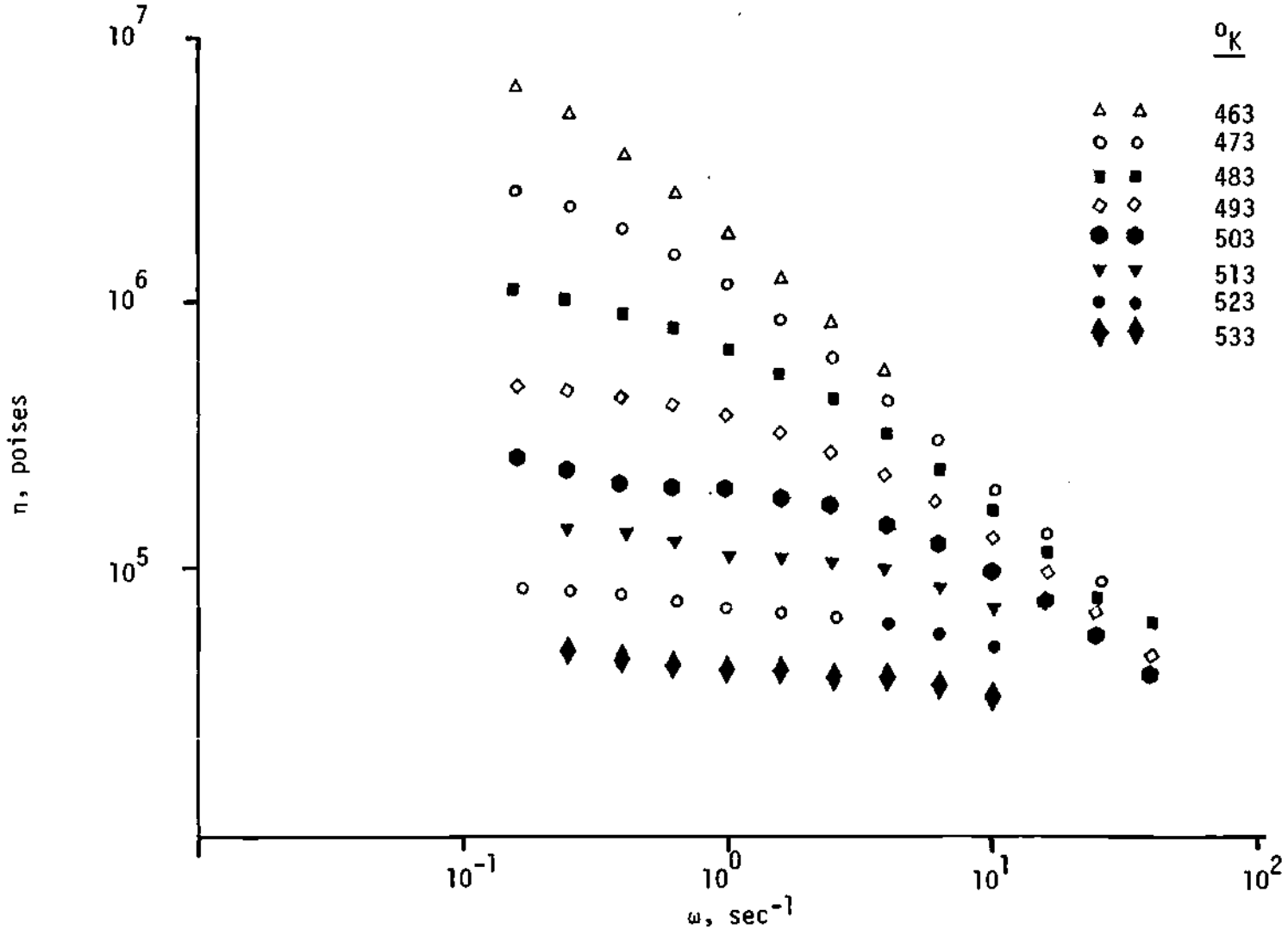


Figure C-3 . Complex, Dynamic Viscosity vs. Frequency for Molecular Weight C, ($\overline{M}_w$)=36,300

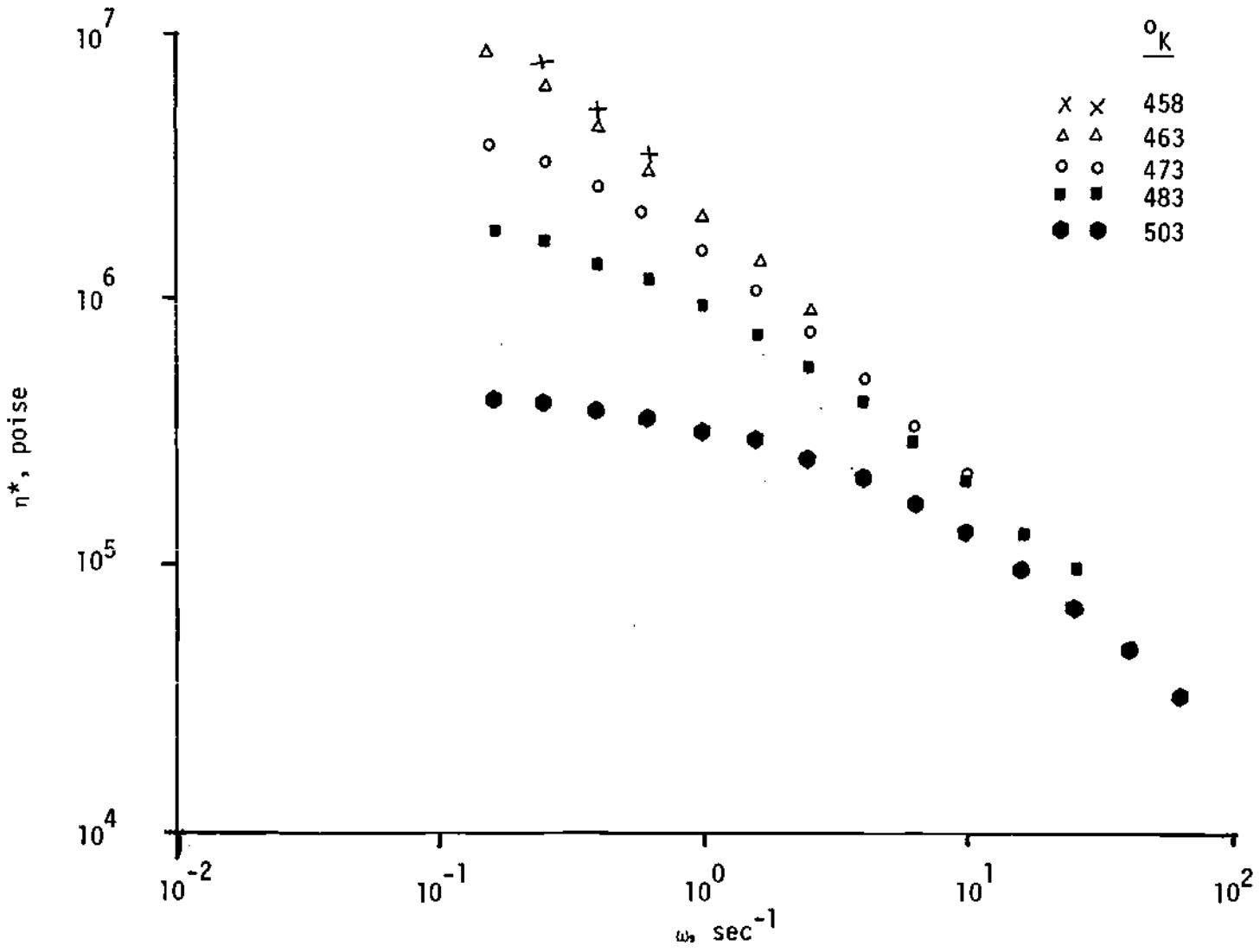


Figure C-4 . Complex, Dynamic Viscosity vs. Frequency for Molecular Weight D, ($\overline{M}_w$)=40,400

BIBLIOGRAPHY

1. L. Boltzmann, Wied. Ann., 5, 430 (1978).

2. J. D. Ferry, Viscoelastic Properties of Polymers (John Wiley & Sons, New York, 1970).

3. A. C. Pipkin, Lectures on Linear Viscoelasticity Theory, Applied Mathematical Sciences 7 (Springer-Verlag, Inc., New York, 1972).

4. G. S. Brockway; Bell Telephone Laboratories, unpublished derivation.

5. C. W. Macosko and J. M. Starita, Society of Plastics Engineers Journal, 27, 38 (November 1971).

6. Dr. F. Kama, Mobay Chemical Corporation, Pittsburgh, Pa., supplied GPC data.

7. J. W. Shea, E. D. Nelson and R. R. Cammons, Society of Plastics Engineers, 33rd Annual Technical Conference Proceedings, 61, 1975.

8. Telephone communication between D. L. Reinhard of Rheometrics, Inc. and V. W. Boehm.

9. S. Onogi, H. Kato, S. Ueki and T. Ibaragi, J. Polymer Science, C-15, 481 (1966).

10. H. Schnell, Chemistry and Physics of Polycarbonates (Interscience Publishers, 1964).

11. Reference 2, p. 304.

12. Reference 2, pl 314.

13. Reference 3, p. 316.

14. J. D. Ferry, J. American Chemical Society, 72, 3746 (1950).

15. S. Strella, J. Polymer Science, 60 S9 (1962).

16. R. A. Mendelson, W. A. Bowles and F. L. Finger, J. Polymer Science, A-2, 8 105 (1970).

17. W. P. Cox and E. H. Merz, J. Polymer Science, 28, 620 (1958).

18. J. W. C. Adamse, H. Janeschitz-Kreigl, J. L. Den Otter and J. S. L. Wales, J. Polymer Science, A-2, 6, 871 (1968).

19. J. D. Ferry, M. L. Williams and D. M. Stern, J. Physical Chemistry, 58, 987 (1954).

20. R. L. Ballman and R. H. M. Simon, J. Polymer Science, A-2, 3557 (1964).

21. F. Bueche, Physical Properties of Polymers, (John Wiley and Sons, New York, 1962).

22. P. E. Rouse, J. Chemical Physics, 21(7), 1272 (1953).

23. R. A. Stratton, J. Colloid and Interface Science, 23, 517 (1966),

24. R. A. Mendelson, W. A. Bowles and F. L. Finger, J. Polymer Science, A-2, 8, 127 (1970).

25. C. H. Hwo and J. F. Johnson, J. Applied Polymer Science, 18, 45 (1974).

26. G. F. Bauman and S. Steingiser, J. Polymer Science, 1, 3395 (1963).

27. J. P. Mercier, J. J. Aklonis, M. Litt and A. V. Tobolsky, J. Applied Polymer Science 9, 447 (1965).

28. M. H. Litt and S. Torp, J. Applied Physics 44, 4282 (1973).

29. J. C. Bauwens, J. Material Science 7, 577 (1972).